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INTERNAL SOLUBILITY IN SOAP MICELLES.

By A. S. C. LAWRENCE.

Received 8th March, 1937.

In a previous paper¹ systematic examination has been made of the peptising action on soap solutions by certain organic substances, first recorded by Lester Smith.² Alcohols, phenols and amines are particularly efficient, but their efficiency depends upon the particular member of each series chosen. At the same time that the soap is peptised, the solubility of the peptiser in the solution is increased largely, in comparison with that in water, until a saturation value is reached. Comparison of substances of the same molecular weight and polar group, such as normal and tertiary amyl alcohols, shows that the saturation value increases with increase of solubility of the peptiser in water alone. For normal amyl alcohol, the saturation value was 6 molecules per molecule of sodium stearate; for tertiary amyl alcohol, 17 and for aniline, 7. As the solubility of the higher members of each series falls off, so does the saturation value for peptisation. Figures could not be obtained for the lower members miscible with water, since the distribution between water and soap cannot be observed. The complexes of soap and peptiser break down on crystallisation. It was proved that the phenomenon was not due to adsorption and that it is a colloidal one. Dipole interaction was suggested as the mechanism by which complexes of soap and peptiser are formed. We are still, however, faced with the difficulty of explaining where the 30 or more methylene groups, or the several benzene rings of the aromatic peptisers, are located. For stability of the complex it is obviously necessary that the exterior should be hydrophilic so that it would seem that the hydrophobic parts of the peptisers are in the paraffin interior of the micelles.

Pickering has found that large amounts of oil can be taken up by concentrated soap solutions.³ He described his mixtures as "true emulsions because water is the external phase"; and, in his second paper, as "emulsions" because the oil droplets were surrounded by solid pellicles of soap. He noted that some of his "emulsions" were optically homogeneous but was misled by his remarkable results on the use of solid powders as emulsifying agents. He succeeded in preparing mixtures of 99 per cent. of oil in soap solution but this was a paste of solid soap and oil rather than a true emulsion.* The text-books all quote this result as a refutation of the phase/volume theory and ignore his further interesting observation that when these mixtures were poured into water part of the oil remained as a stable oil/soap

¹ A. S. C. Lawrence, *Faraday Soc. Trans.*, 1937, **33**, 325; *P.R.S.*, 1935, 59.

² *J. Physic. Chem.*, 1932, **36**, 1401.

³ *Chem. Soc. J.*, 1907, 2001 and 1917, 95.

* See p. 817.

sol and only part separated as emulsion.* He carried out analyses by an indirect method and showed that oil was dissolved in the diluted soap sol.

Pickering's work has been repeated and complete direct analyses made of these curious systems. Further observations have been made which clearly indicate that they involve internal solution in the hydrocarbon interior of the soap micelles.

Analysis is simple, except that the usual method for determination of unsaponifiable matter (extraction by petrol ether from solution of the soap in 50 per cent. alcohol-water mixture) cannot be used. Addition of the necessary alcohol to the soap/oil/water systems precipitates a semi-solid mixture of oil and soap and not the unsaponifiable oil alone. The following procedure was therefore used. Soap solution was made up from 28.2 gm. of Oleic acid, 5.6 gm. of KOH and 128 c.c. of water; that is 20 per cent. solution of soap. In this, 80 c.c. of Nujol was incorporated by stirring. The changes of the consistency of the mixture which take place are described by Pickering. The mixture was then diluted with about 1 litre of water and left to stand. After several days 150 c.c. of emulsion had "creamed" and 840 c.c. of slightly opaque sol remained. The emulsion was separated, carrying with it 27 c.c. of the sol, and cracked by addition of acetic acid; 68.2 c.c. of oil separated and was washed until the washings were free from acid. The use of warm water made possible quick and sharp separation of the oil. This consists of Nujol and oleic acid from the emulsifying layer and entrained sol. It was then titrated in 50 per cent. alcohol/water solution against KOH using phenol phthalein as indicator. The KOH was standardised against the oleic acid used.

10 gm. oleic acid required 65.6 c.c. KOH.

68.2 c.c. of oil from cracked emulsion required 22.8 c.c. which is equivalent to 3.45 gm. of oleic acid.

The oil therefore contained 64 c.c. of Nujol and the remaining 16 c.c. were in the sol associated with 24.75 gm. of oleic acid as potassium soap.

250 c.c. of the sol were then taken, decomposed by acetic acid and the oil extracted by petrol ether. The extract, after washing till free from acid, was titrated in the same manner and required 43.2 c.c. of KOH. This was equivalent to 6.59 gm. of oleic acid. The 813 c.c. therefore contained 22.2 gm. of soap together with 16 c.c. of Nujol. (This is not the maximum amount that could be taken up.) Analyses were made on systems containing more oil but the results were not so accurate since separation was less sharp.

The emulsion consisted of 64 c.c. of Nujol in 81.2 c.c. of soap solution. The latter alone would contain 2.48 gm. of soap but actually contained 4.86, the difference of 2.38 gm. being that adsorbed in the emulsifying layer. A monolayer of soap on 64 c.c. of Nujol dispersed in droplets of 1μ diameter requires 1.14 gm. of soap, taking the area per soap molecule as 20 \AA.U.^2 .

Alternative Methods for Incorporating Oil.

Pickering prepared his soap/oil/water systems by stirring the oil into concentrated soap solution, a method that has the disadvantage of emulsifying some of the oil at the same time. Two alternative methods have been found which are free from this difficulty. Oil can be incorporated in the soap which is then dissolved in water. Pickering extrapolated the linear relation between amount of oil taken up and concentration of soap to find how much the dry soap would take up alone. Very little, however, was absorbed instead of the large calculated amount; this is due to the

* "Colloid Chemistry," A. W. Thomas, 1934, is an exception.

high temperature of dispersion of soap in oil or oil in soap. For sodium soaps this is about 180° and for potassium 230° . His oils all had boiling-points below these temperatures. If equal weights of soap and Nujol are heated until a clear liquid, solid soap is formed on cooling: this can be powdered and then dissolves readily in warm water. Alternatively the oil may be mixed with fatty acid—oleic is particularly convenient being a liquid—and the mixture saponified.

By this second method substances other than oils can be incorporated. Water-insoluble dyes, such as Scharlach R, remain dissolved in the soap-in-water indefinitely, provided sufficient water is allowed. One such sol prepared in 1932 has deposited no solid. Silver stearate, which is normally insoluble in water, is incorporated in the same way. It forms a sol which shows very marked streaming optical properties. In this case, the micelle has clearly developed crystalline structure. In this respect internal solution differs from peptisation in that peptised complexes are broken down by solidification. The silver stearate is presumably not all dissolved in the interior of the micelles owing to the smallness of its solubility in the paraffin chains at room temperature, whereas at higher temperatures it is dissolved to a clear sol without streaming effects.

The Nature of the Systems.

Pickering found that his mixtures sometimes formed lumps of "clear gel" on standing. One of these was examined under the microscope and was clearly not an emulsion. Tested by oil soluble dye, it appeared to be homogeneous but in polarised light, very thin crystalline plates of soap could be detected. His 99 per cent. oil "emulsion" is in fact a paste of oil and solid soap. When the oil is first added to the concentrated soap solution, oil is absorbed until the saturation value is reached; the complex is less soluble than the original soap and separates as solid which then forms a paste with more oil. Pickering's method of analysis contains an error which becomes serious with these very high oil contents. The cracked oil whose volume he measured contains oleic acid from the emulsifying layer and he included this in the total oil content, only allowing for the minute amount of soap in the residual 1 per cent. of soap solution.* His method of preparation is unsuited for determination of saturation of the soap by oil; in fact, he considered that the amount taken up varied with the concentration but this effect was probably due to the emulsification which always proceeds alongside of the incorporation and to the fact that dilute solutions of soap are very slow in taking up the oil since it has to penetrate the hydrophilic exterior of the micelles. It appears that the amounts of various oils taken up by a given solution are all of the same order and do not vary with the molecular weight of the oil. Thus, much the same amounts of benzene and of Nujol are dissolved in spite of very large difference of molecular weight. There is no continuity between emulsions and soap micelles containing internally dissolved oil. The smallest droplets in emulsions are very large compared with the soap micelle containing oil but it is difficult to observe the saturation value for the amount of oil dissolved inside the micelle. This determination, however, can be made with soap dissolved in 90 per cent. alcohol by adding Nujol to the hot soap solution. In the absence of soap the Nujol is not soluble. To the solution of a known amount of soap Nujol is therefore added until no more is dissolved. These solutions are comparable with aqueous ones since the soap is colloiddally dissolved. The saturation values for 10 gm. of sodium stearate dissolved in 200 c.c. of alcohol were:

* On the basis of the analysis above, the oleic acid in Pickering's emulsion would be 3.82 gm. so that the oil content is reduced from 99 per cent. to 95.2 per cent.

Potassium stearate	.	.	17 gm. Nujol
Sodium stearate	.	.	11 " "
Cæsium stearate	.	.	20 " "
Sodium laurate	.	.	8 " "

Bury has shown by determinations of the partial specific volume of potassium octoate in water that the colloid particles are somewhat loosely packed.⁴ However, absorption of the amounts of liquids described above requires swelling. This swelling is limited, probably as Hartley has suggested,⁵ by the constriction of the particles by the exterior water. Swelling can take place so long as the exterior of the micelle remains hydrophilic; that is, so long as the polar groups of the soap micelle are not separated too far. It is in agreement with this view that the amounts of oil taken up by the alkali soaps, Na, K, Cs, increase with increase of size of ion. The smaller value of the laurate compared with the stearate is of course due to the smaller amount of internal hydrocarbon available as solvent.

This picture of internal solution of oils and oil-soluble substances in the hydrocarbon interior of the soap micelle means that the polar exterior is unaffected chemically and merely plays the part of a container for the solvent hydrocarbon. Three observations were made which support this view. Soap containing Nujol or Scharlach R was precipitated as barium soap. In each case the internally dissolved substance was carried down with the precipitate but was not held in it as a stable system since both oil and dye were extracted by cold petrol ether. Again, chromates and chlorides formed no precipitate when added to the sodium soap sol containing internally dissolved silver stearate. In this case, however, vigorous boiling produced precipitates. The barium soap precipitated from the oil/soap sol rose to the surface whereas in absence of oil it sinks. On the other hand the oil internally dissolved in potassium stearate micelles causes an increase in their density.

Conclusion.

The absorption of organic substances by colloidal soap solutions can take place by two quite different methods. First, water-soluble substances containing one or more polar groups attach themselves to the exterior of the soap micelle by dipole interaction. The soap is peptised. (Fig. 1.)

Second, by internal solution of paraffin-soluble substances in the hydrocarbon interior of the soap micelles. Here there is no peptisation. (Fig. 2.) Actually in many cases both mechanisms operate since the majority of organic molecules are oil-soluble but also contain polar groups. The polar groups then lie in the surface of the micelles by mechanism 1 while the hydrophobic portion of the molecule is internally dissolved by mechanism 2. If the absorbed molecule is not very large there may still remain space in the centre of the micelle for further internal solution. Amyl alcohol and aniline in sodium stearate show this last case well. (Fig. 3.) About 3.5 molecules of aniline are absorbed per molecule of soap by mechanism 1. At this point the setting-point of the soap, which depends on the nature of the polar exterior of the micelles, has become asymptotic and the further 3.5 molecules of aniline which are taken up before saturation is reached exert no lowering on the setting-point.* These are, therefore, presumably internally dissolved by mechanism 2. The end point of mechanism 2 is much less

⁴ *Chem. Soc. J.*, 1930, 2263; also 1929, 679.

⁵ Hartley, G. S., *Aqueous Solutions of Paraffin-chain Salts*, 1936, p. 45.

* Ref. 1 (Fig. 3).

sharp than that of mechanism 1, owing no doubt to the fact that the

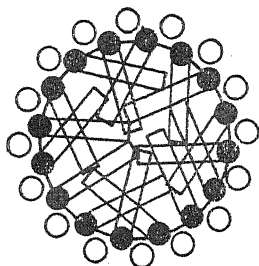


FIG. 1.—Surface absorption of water-soluble, hydrocarbon-insoluble substances by dipole interaction of the polar groups. Soap is peptised. Examples: sugars, starch, glycerol.

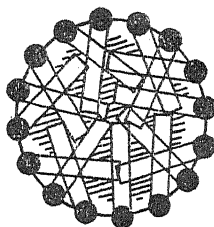


FIG. 2.—Internal solution of water-insoluble, hydrocarbon-soluble substances such as hydrocarbons.

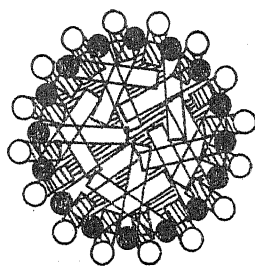


FIG. 3.—Both mechanisms operating simultaneously in case of substances, such as amyl alcohol or aniline, which contain both polar groups and hydrocarbon residues. The substance dissolved in the centre of the micelle is by internal solution without dipole interaction, although it contains polar groups but these are out of contact with the polar groups of the soap which are all at the surface, to which short molecules do not all reach.

substance absorbed is hydrophobic and has to penetrate the hydrophilic surface layer of the micelle.

In cases where the peptiser is taken up by both mechanisms, it is possible that saturation will be limited by the capacity of the micelle to dissolve the hydrophobic parts of the peptisers. The saturation values for substances such as aniline and amyl alcohol should, then, be of the same order as the saturation values for oil internally dissolved. The results are:

Nujol	.	.	.	1.1 gm./gm. sodium stearate
Aniline	.	.	.	2.13 " " "
<i>n</i> -Amyl alcohol	.	.	.	1.72 " " "
Tertiary Amyl alcohol	.	.	.	4.87 " " "

The higher values where peptisation occurs suggest that in these cases saturation is not limited only by the internal solubility. This agrees with the fact previously noted that the amount of a given peptiser taken up at saturation by the homologous sodium soaps increases as the chain length decreases.

Detergence.

As Pickering pointed out, this property of internal solution of oil suggests that for maximum efficiency of removal of dirt, a concentrated soap solution should be used so that most of the dirt would be removed as stable sol instead of as less stable emulsion. It is obvious that this only applies to liquid dirt. Nor would it apply to cases in which the amount of oil to be removed was large; since then the amount of soap required to carry away the oil as sol would be enormous compared with that required to remove it as emulsion. From the alternative methods of preparation of these soap/oil complexes, it would appear that the best way to remove dirt in reasonably small amount would be by rubbing fatty acid into the fabric and subsequently saponifying. I understand that a patent has been taken out for this method on empirical grounds. Pickering's suggestion of the use of concentrated soap solution suffers

from the disadvantage that the soap in it is not so readily available for formation of monolayers around such dirt as is removed as protected suspension or emulsion. It is obvious that the detergent should be readily soluble in water so that it is available in molecular dispersion for formation of monolayers; and also to increase the solubility of any complexes formed from the liquid dirt. The experiments with barium salts show that soft water is necessary since the precipitated soaps containing oil are peculiarly adherent. Washing one's hands when oily illustrates this well. The oily precipitate sticks to the basin around the surface of the water in an unmistakable way.

Summary.

Oils and oil-soluble substances are dissolved in the interior of soap micelles which consist of the hydrocarbon tails of the soap molecules and which therefore act as a hydrocarbon solvent. The oil thus attains an apparent solubility in water. There is a definite saturation value for the amount of oil taken up. This is much smaller than the smallest droplet of an emulsion and there is no continuity between the two systems. The amount of oil taken up is of the same order for a given soap irrespective of molecular weight. The amount of solid solutes internally dissolved is limited by their solubility in the paraffin-interior. Hartley has described experiments to show that this solubility is that in paraffin in bulk.⁶

The work described above forms part of certain investigations undertaken for the Fuel Research Division of the Department of Scientific and Industrial Research. It was carried out in the Laboratory of Colloid Science, Cambridge, by kind permission of Professor E. K. Rideal to whom I am grateful for his helpful interest in my work.

⁶ Hartley, G. S., *Leather Trades' Chemists' Symposium* on "Wetting and Detergence," 1937 (report in press).

THE EQUILIBRIUM BETWEEN HYDROGEN SULPHIDE AND HEAVY WATER.

BY P. A. SMALL.

Received 19th April, 1937.

The purpose of this work was to measure the equilibrium constant for the reaction $\text{H}_2\text{S} + \text{HDO} = \text{HDS} + \text{H}_2\text{O}$ and compare the value obtained with that calculated from spectroscopic data. Since the method used for estimating deuterium concentrations of heavy water was only useful for the range 0.5 per cent., it was not feasible to measure other constants of the system hydrogen sulphide plus heavy water.

Experimental.

A weighed amount of water of known deuterium constant was brought into reaction with hydrogen sulphide in a vessel of known volume at a measured pressure, and the change in deuterium content was determined.

The reaction vessel was a pyrex flask of $1\frac{1}{2}$ - $2\frac{1}{2}$ litres capacity, provided with a side tube for the entry of gas, and an appendix some 12 cm. long by 12 mm. diameter was fused onto the drawn out neck, in which the water was frozen out during the admission and withdrawal of the gas. It was

connected when required to a vacuum system with manometer, and a trap in which the hydrogen sulphide was stored as a solid. (Fig. 1.)

The hydrogen sulphide used in this reaction was prepared by dropping hydrochloric acid onto crystals of sodium sulphide, and was washed with water to remove hydrogen chloride, dried with phosphorus pentoxide, and stored by freezing with liquid air.

The method of procedure was briefly as follows: The heavy water of deuterium content 4.5 per cent. was weighed into the cleaned and

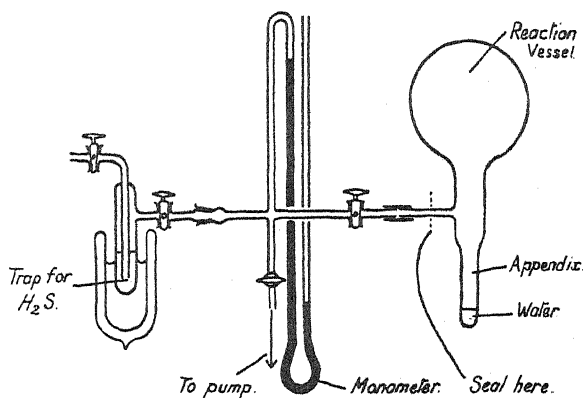


FIG. 1.

dried reaction vessel from a specially designed weight pipette, in such a manner that it dropped into the appendix, and not on to the walls of the vessel. The water was frozen out, and the vessel was connected to the vacuum system and pumped out, the loss of water being negligible. Hydrogen sulphide was then allowed to evaporate into the vessel, which was then warmed up to room temperature, the freezing mixture being removed from the appendix. When the whole vessel had attained room temperature, the pressure of gas was measured and the side tube sealed off. The vessel was inverted so that the water drained down into the bulb, presenting a large surface for the heterogeneous interchange. It was found in preliminary experiments that very slight traces of grease markedly hindered the reaction, by covering the surface.

When the reaction was complete, the vessel was again inverted and a freezing mixture applied to the appendix, so that the water drained and distilled back, and was frozen out. The vessel was again connected to the vacuum system, and the hydrogen sulphide pumped off, or distilled back into the trap. The appendix was cut off with the frozen water in it. To remove traces of hydrogen sulphide dissolved in the water it was distilled *in vacuo*, in an apparatus figured in a previous paper.¹ It was then treated with a small amount ($\frac{1}{2}$ g.) of dried mercuric oxide to remove final traces of hydrogen sulphide, and redistilled. It was shown in blank experiments using ordinary water that this procedure was efficient in removing hydrogen sulphide, leaving the density of ordinary water unchanged.

The deuterium content of the water was estimated by determining its density, using a float and varying the temperature according to the method already described. As a check on the purity of the water each specimen was redistilled and the density redetermined.

To test whether a true equilibrium was reached, a back exchange was done, approaching the equilibrium from the other side. A specimen of hydrogen sulphide from a previous run was used, with an enhanced and known deuterium content, and ordinary distilled water was used in place of heavy water. In collecting the gas in the trap, a phosphorus pentoxide tube was inserted between the reaction vessel and the vacuum system. The value found in this run agreed well with the others.

¹ Small and Wolfenden, *J.C.S.*, 1936, 1811.

Results and Discussion.

The concentration of deuterium in the gas is found from the drop in deuterium content of the water. To calculate the equilibrium constant it is necessary to know the separate concentrations of all the molecular species present; for this purpose the constant $K_1 = (\text{HDO})^2/(\text{H}_2\text{O})(\text{D}_2\text{O})$ and the corresponding one for the different isotopic forms of hydrogen sulphide must be known. Topley and Eyring² calculated the former to be 3.24 at 15° C. A value of four was taken for the latter; the concentrations found for the species HDS and HDO are not sensitive to the precise values assigned to these constants in the range of deuterium concentrations being considered.

TABLE I.—EXPERIMENTAL RESULTS.

Run Number.	1.	2.	3.	4.	5. (Back Reaction.)
Mols. of Gas .	0.1015	0.0990	0.100	0.0592	0.0890
Mols. of Water .	0.185	0.273	0.1175	0.1415	0.146
Initial D content of gas (per cent.)	—	—	—	—	2.00
Initial D content of water (per cent.)	5.364	5.364	4.099	4.099	0.02
Final D content of water (per cent.)	4.385	4.637	2.993	3.494	0.930
Constant for hetero- geneous reaction	0.397	0.428	0.405	0.430	0.450
Time in days .	2	2	20	20	2

The mean value found for the constant for the heterogeneous reaction, $\text{H}_2\text{S}_{\text{gas}} + \text{HDO}_{\text{liq.}} = \text{HDS}_{\text{gas}} + \text{H}_2\text{O}_{\text{liq.}}$, was 0.422 ± 0.019 .

To obtain from this result the value of the constant for the reaction occurring entirely in the gas phase it is necessary to multiply by the factor $\frac{(\text{HDO})_{\text{liq.}}(\text{H}_2\text{O})_{\text{gas}}}{(\text{H}_2\text{O})_{\text{liq.}}(\text{HDO})_{\text{gas}}}$. Assuming Henry's law, this is the ratio of the vapour pressures of H_2O and HDO . The vapour pressure of HDO is taken, following Topley and Eyring,² as the geometric mean of those of H_2O and D_2O , and using the data of Wahl and Urey³ this factor has the value 1.075 at 15° C.

The value of the constant for the reaction in the gas phase becomes 0.453 ± 0.020 at 15° C.

The general expression⁴ for the equilibrium constant for a reaction of this type is:—

$$\log_e K = -\frac{\Delta E}{RT} + \frac{3}{2}\sum \log_e M + \frac{1}{2}\sum \log_e (I_A I_B I_C),$$

where ΔE is the change in zero-point energy for the reaction, the M 's are the molecular weights, and the I 's are the moments of inertia for the molecules, the summation being taken counting the reactants negative and the resultants positive. The moments of inertia for the isotopic molecules were calculated treating them as rigid planar structures and using the configurations and dimensions given by Spomer;⁵ these were assumed to be unaltered by substitution of deuterium for protium.

² Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 217.

³ Wahl and Urey, *ibid.*, 1935, **3**, 411.

⁴ Giauque, *J.A.C.S.*, 1930, **52**, 4808.

⁵ Spomer, *Molekülspektren*, 1935, Berlin.

When the experimental part of this work was done, no analysis had been made of the spectra of the isotopic hydrogen sulphides, and it was therefore necessary to calculate their vibration frequencies, which was done using the equations given by Ellis and Sorge ⁶ for a simple central force system. Though the absorption spectra of the hydrogen sulphides have now been investigated,⁷ and values may be obtained for the zero-point energies from the data published, the calculated values are retained, as it is of interest that in the case of simple molecules like those under consideration, such good results can be obtained by a relatively simple method of calculation, from a knowledge solely of the properties of the molecules containing protium.

In Table II. below, the first set of values for H₂S and HDS are derived from the vibration frequencies calculated as indicated above, and the second set are derived from the published results of the actual analysis of the spectra, making allowance for the effect of anharmonicity. The corresponding values for the zero-point energy difference and constant for the reaction in the gas phase are placed alongside. The values used for the water molecules are derived from the values calculated by Topley and Eyring for the vibration frequencies, allowing a half-quantum per vibrational mode.

In an exchange reaction where the molecules taking part are fairly large, the terms arising from the differences in molecular weight and moment of inertia are small. The values found for the second and third terms are + 0.0356 and - 0.0353 respectively, so that they cancel out almost exactly, and the free energy of the reaction becomes identical with the difference in zero-point energy :

$$\Delta F = - RT \log_e K = \Delta E$$

Summary.

The heterogeneous exchange equilibrium between heavy water and hydrogen sulphide is measured at 15° C., and the homogeneous equilibrium constant in the gas phase calculated from the result. The value obtained is compared with the values derived from calculations of zero-point energy and from spectroscopic data.

⁶ Ellis and Sorge, *J. Chem. Physics*, 1934, **2**, 556.

⁷ Bailey, Thompson, and Hale, *ibid.*, 1936, **4**, 625.

Exeter College,
Oxford.

TABLE II.—MOLECULAR DATA.*

Molecule.	I_A .	I_B .	I_C .	Zero-point Energy.	ΔE .	K Calc.
H ₂ O	1.03	1.97	3.00	13104		
HDO	1.22	3.14	4.36	11330		
H ₂ S	2.75	3.15	5.90	9296 †	479 §	0.436
				9515 ‡		
HDS	3.17	5.49	8.66	8001 †	463	0.448
				8204 ‡		

* I 's in gm. cm.² $\times 10^{-40}$ and zero-point energies in Cals./Mol.

† Calculated.

‡ From spectra.

§ From calculated zero-point energies.

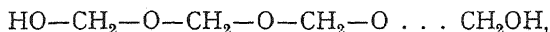
|| From zero-point energies derived from spectra.

MAGNETISM AND POLYMERISATION. 2. THE OXYMETHYLENE DIACETATES AND THE POLYOXYMETHYLENES.

BY JOHN FARQUHARSON.

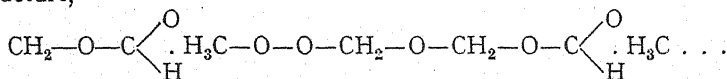
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According to Staudinger¹ the Polyoxymethylenes are long chain compounds, α and β polyoxymethylene being dihydrates of the type,

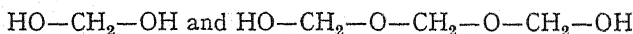


the average number of CH_2O groups per molecule being very large, probably over one hundred, and larger for β than α polyoxymethylene. The structures of γ and δ polyoxymethylene are uncertain but they are supposed to be dimethyl ethers as they are only formed in the presence of methyl alcohol. X-ray evidence shows also that γ and δ polyoxymethylene contain a number of $-\text{C}-\text{C}-$ linkages and so they cannot have quite the same structure as α and β .

Good² has measured the magnetic susceptibilities of solutions of formaldehyde in water and also of the solid poly-oxymethylenes. He applied Pascal's atomic values to long chain molecules of the type shown above, but found that he could get no agreement between the values so calculated and his experimental results. He therefore suggested the structure,



where the dots indicate some loose form of binding between the component parts of the large aggregate. As aldehydic oxygen was shown by Pascal to lower the diamagnetic susceptibility of a molecule, Good was thus able to explain why his experimental results should be so much lower than the values calculated on the assumption of the long chain structure for the polyoxymethylenes. Also, his measurements of formaldehyde solutions agreed with the suggestion put forward by Auerbach and Barshall that the solutions contain molecules of the type



Although Pascal's atomic values give good agreement with experiment in many instances, they do not always do so, and it is the susceptibilities of groups of atoms which are more likely to give additive values than the susceptibilities of the atoms themselves. If this is taken into account it can be shown that the magnetic evidence supports Staudinger's view as to the structure of the α and β polymers.

The Susceptibilities of a Homologous Series.

In a previous paper³ it was shown that when a substance polymerises, the mass susceptibilities of the sequence of polymerides lie on a hyperbola,

¹ Staudinger, *Die Hochmolekularen Organischen Verbindungen*, p. 279.

² Good, *J. Roy. Tech. Coll. Glasgow*, 1931, 2, 401.

³ Farquharson, *Trans. Faraday Soc.*, 1936, 32, 219.

whilst their molecular susceptibilities should lie on a straight line. In a homologous series, Pascal's additivity results show that the molecular susceptibilities should also lie on a straight line. The mass susceptibilities will again lie on a hyperbola because of the end groups having susceptibilities differing from the susceptibility of the recurring group. The limiting value of the susceptibility will be that of the recurring group. This is very well demonstrated by Cabrera and Fahlenbrach's measurements of the alcohols.⁴

The formula which was given in the previous paper for the mass susceptibilities of a series of polymers,

$$\chi = \frac{n\chi_B + (n-1)\lambda}{nM_B}$$

can also be written in the form,

$$\chi = \frac{\chi_B + (n-1)\chi_C}{nM_B}$$

where χ_C is the susceptibility of the group which is added each time to give the next higher polymeride for, λ , the bond change, is simply $\chi_C - \chi_B$. In a homologous series the same type of relationship will hold except that nM_B is modified to $M_B + (n-1)M_C$ where M_B is the molecular weight of the first member of the series and M_C is the molecular weight of the added group, *i.e.*, the mass susceptibilities of a homologous series is given by the expression

$$\chi = \frac{\chi_B + (n-1)\chi_C}{M_B + (n-1)M_C}$$

Thus by measuring χ and knowing χ_B , χ_C , M_B and M_C it should be possible to find n , the number of added groups, provided n is not very large.

Experimental.

The Susceptibility of the $-\text{CH}_2\text{O}-$ Group in Combination.—The susceptibilities of the groups $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{O}- \\ | \\ \text{H} \end{array}$ and $\begin{array}{c} \text{H} \\ | \\ -\text{C}- \\ | \\ \text{O} \\ | \\ \text{H} \end{array}$ are the same if cal-

culated on the basis of Pascal's atomic values namely 16.5 (C, 6.0; O, 4.6; H, 2.95). If series of compounds containing these different groups are measured, however, it is found that the group susceptibilities are different, and it is this which explains Good's failure to find agreement between the chemical and magnetic results for the polymethylenes.

An estimate of the susceptibility of the

$\begin{array}{c} | \\ \text{H}-\text{C}-\text{O}-\text{H} \\ | \end{array}$ groups

TABLE I.—THE SUSCEPTIBILITIES OF SOME POLYHYDRIC ALCOHOLS AND OF THE $\begin{array}{c} | \\ \text{H}-\text{C}-\text{O}-\text{H} \\ | \end{array}$ GROUP IN COMBINATION.

	Number of $\begin{array}{c} \\ \text{H}-\text{C}-\text{O}-\text{H} \\ \end{array}$ Groups.	$-\chi_M \times 10^6$.	Δ .	Suscep- tibility of $\begin{array}{c} \\ \text{H}-\text{C}-\text{O}-\text{H} \\ \end{array}$
Glycerol .	1	56.9	16.8	16.6
Erythritol .	2	73.7	32.9	
Mannitol .	4	106.6		

⁴ Cabrera and Fahlenbrach, *Z. Physik*, 1933, 85, 568.

was made by measuring the susceptibilities of some polyhydric alcohols as shown in Table I. This shows very close agreement with Pascal's value.

Measurements of the oxymethylene diacetates, however, give a value for $-\text{CH}_2-\text{O}-$ which is a good deal lower than this. The results for some of them are given in Table II. The molecular susceptibilities of the diacetates lie on a straight line and the value per $-\text{CH}_2\text{O}-$ group calculated by the method of least squares is -14.87×10^{-6} .

The polyhydric alcohols were as supplied by B.D.H. Ltd., the glycerol being A.R. The oxymethylene diacetates were prepared by the method of Signer⁵ by heating together in sealed tubes paraformaldehyde and acetic anhydride in the proportions of 1 : 5. The diacetates were separated by extracting the mass with different solvents. The lower members were separated by fractional distillation under reduced pressure and the higher members by fractional crystallisation. All the measurements were made on a Gouy apparatus and are accurate to at least 0.5 per cent.

α - and β -Polyoxymethylenes.—The mass susceptibility of $-\text{CH}_2\text{O}-$ in the oxymethylene diacetates calculated from the average value for the molecular susceptibility is 0.496×10^{-6} . If the polyoxymethylenes were long chain molecules made up of many $-\text{CH}_2\text{O}-$ units their susceptibilities should be somewhere near this value since the mass susceptibility curve would approach this figure, no matter what the end groups are, as

TABLE II.—THE SUSCEPTIBILITIES OF THE OXYMETHYLENE DIACETATES.

Number of $-\text{CH}_2\text{O}-$ Groups.	$-\chi_M \times 10^6$.
1	70.7
2	85.8
3	100.5
4	115.6
6	145.2
9	190.6
22	383.0

TABLE III.—GOOD'S RESULTS FOR THE POLYOXYMETHYLENES.

	Mass Susceptibility $-\chi \times 10^6$.
α polyoxymethylene	0.503
β „	0.501
γ „	0.467
δ „	0.417

n becomes very large. Good's results, shown in Table III., thus indicate that only α - and β -polyoxymethylenes are long chain compounds of this type; the structures of the other polymers are probably fundamentally different.

The best method of applying the formula in order to find the number of groups in the α and β polymers would be to measure the susceptibilities of a series of dihydrates similar to the series of diacetates. The dihydrates have never been isolated, but it is very unlikely that the value for $-\text{CH}_2\text{O}-$ in the series of hydrates is different from the value in the series of diacetates. This being so then it is only necessary to arrive at a value for the susceptibility of the first member of the series, $\text{HO}-\text{CH}_2-\text{OH}$, and then apply the formula. Since the dihydrates and the diacetates are very similar molecules, it is probable that the magnetic contribution of the bonds between H_2O and CH_2O in the dihydrates is the same as the contribution of the bonds between $(\text{CH}_3\text{COO})_2\text{O}$ and CH_2O in the diacetates, so that if the susceptibility of acetic anhydride is subtracted from the susceptibility of oxymethylene diacetate and that of water added, then the value for methylene glycol so obtained will be very nearly the correct one. If this is done then the susceptibility of $\text{HO}-\text{CH}_2-\text{OH}$ is -31.0×10^6 .

If the formula is now applied to the susceptibilities of the α and β

⁵ Signer, *Dissertation, Zurich E.T.H.*, 1927.

polymers, using this value for the susceptibility of the first member of the series, the results are

α polyoxymethylene $n = 32$ Molecular weight = 978
 β polyoxymethylene $n = 44$ Molecular weight = 1338.

The magnetic investigation thus leads to the result that α and β polyoxymethylene are both dihydrates and that the molecules of the β polymer contain a higher average number of $-\text{CH}_2\text{O}-$ groups than do the molecules of the α polymer. This is in qualitative agreement with the suggestions of Staudinger but the quantitative result is much smaller than he suggests. According to Signer, α polyoxymethylene requires heating *in vacuo* to 100°C . before the aldehyde content can be raised to 99 per cent. The average molecular weight just found gives an aldehyde content of 98.3 per cent.

γ - and δ -Polyoxymethylenes.—It is obvious from the magnetic results that the γ and δ polymers are different from the α and β . They certainly cannot be composed of $-\text{CH}_2\text{O}-$ units for then their susceptibilities would be of the order of 0.496. The X-ray evidence that they contain $-\text{C}-\text{C}-$ linkages also points in this direction. Also, if they do contain these linkages they cannot be of the type found in the polyhydric alcohols because this would have the effect of raising the susceptibility still higher and experiment shows it to be lower. It is hoped that some light may be thrown on this problem by a similar study of the oxymethylene dimethylethers.

Summary.

A magnetic study of the polyoxymethylene diacetates gives a value for the $-\text{CH}_2\text{O}-$ group in combination which is smaller than would be expected from Pascal's additivity rule.

By means of this value it is possible to estimate the number of $-\text{CH}_2\text{O}-$ groups in α and β polyoxymethylenes.

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THE CATALYTIC INTERACTION OF HEAVY HYDROGEN AND BENZENE ON PLATINUM.

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In a previous paper¹ it has been shown that the catalytic hydrogenation of ethylene by heavy hydrogen is accompanied by an exchange of hydrogen atoms between ethylene and heavy hydrogen. Similar reactions take place also between liquid benzene and heavy hydrogen.² In the present paper the catalytic interaction of benzene and heavy hydrogen was investigated in the gaseous phase³ in order to obtain some information about this simple hydrogenation process and whether there is any connection between the exchange and the hydrogenation reaction. It was suggested by Horiuti and Polanyi⁴ that in the catalytic interaction of liquid benzene and heavy hydrogen there is such a

¹ A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc., A*, 1934, 146, 630.

² J. Horiuti, G. Ogden and M. Polanyi, *Trans. Faraday Soc.*, 1934, 30, 663.

³ A. Farkas and L. Farkas, *ibid.*, 1937, 33, 678.

⁴ I. Horiuti and M. Polanyi, *ibid.*, 1934, 30, 1164.

connection between hydrogenation and exchange, since both reactions are claimed to involve the "half-hydrogenated" state.

1. Experimental.

The experimental arrangement was the same as used in the investigation of the exchange reactions between water or alcohol and heavy hydrogen.³ A platinised platinum foil was used as catalyst sealed into the reaction vessel. The benzene was kept in one limb of the reaction vessel in such a way that only its vapour came into contact with the

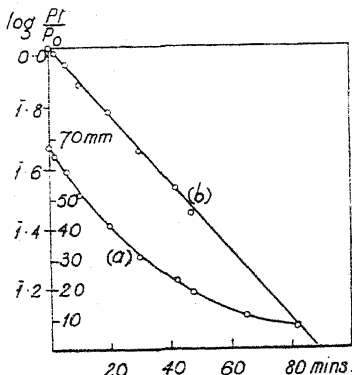


FIG. 1.—Progress of the Hydrogenation. Expt. No. 55 : 59 mm. C_6H_6 + 67 mm.

D_2 . Curve (a) : Pressure of hydrogen in mm. Hg. Curve (b) : $\log P/P_0$.

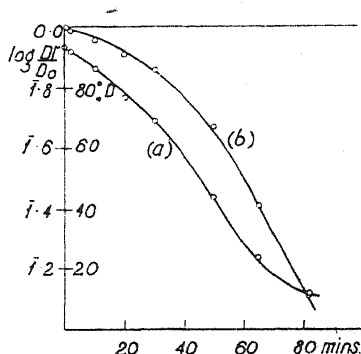


FIG. 2.—Progress of the Exchange. Expt. No. 55 : 59 mm. C_6H_6 + 67 mm. D_2 .

Curve (a) : D-content in per cent. Curve (b) : $\log D/D_0$.

catalyst. The vapour pressure of benzene was adjusted by different temperature baths. The exchange reaction was followed up in the usual way by the microconductivity method.⁵

2. The Progress of the Hydrogenation and Exchange with Time.

In each experiment the course of the reaction was followed up carefully, and Figs. 1 and 2 give typical examples of the hydrogenation and exchange.

The rate of uptake of hydrogen is practically proportional to the pressure (P) of hydrogen as becomes evident if $\log P/P_0$ is plotted against time. On the other hand the progress of the exchange reaction $C_6H_6 + HD \rightleftharpoons C_6H_5D + H_2$ is not obeying such a simple rule as has been found in exchange reactions which are not accompanied by a hydrogenation reaction. For example, in the exchange reaction between H_2O vapour and D_2 ,³ it was found that for practical purposes the decrease of the D-content of the heavy

TABLE I.

Mins.	Pressure (P) in mm.	Tangent $\frac{d \ln D}{dt}$.	$P \cdot \frac{d \ln D}{dt}$.
2	64	0.0091	0.703
10	51	0.0111	0.566
20	41	0.0135	0.553
30	31	0.0168	0.520
42	23	0.0223	0.514
65	11	0.0431	0.476

hydrogen proceeds according to $D_t = D_0 e^{-kt}$ where D_t and D_0 are the

⁵ A. Farkas and L. Farkas, *Proc. Roy Soc., A*, 1934, 144, 467.

D-content at the time t and $t = 0$, and k the relative velocity constant which is connected with the absolute velocity constant k_a by $k_a = kP_{D_2}$. (The absolute velocity constant is proportional to the number of H atoms or molecules exchanged per unit of time.) In the exchange reaction with C_6H_6 , however, the velocity constant k , being dependent on the hydrogen pressure changes in the course of the reaction, since the hydrogen is being used up by the hydrogenation reaction. If one plots $\log \bar{D}_t/\bar{D}_0$ in dependence of time, the tangent of this curve will be proportional to the relative reaction velocity.

In Table I the tangents of this curve are listed with the actual hydrogen pressures, and it will be recognised that the product of tangent \times hydrogen pressure (Column 3) changes only little with the pressure. Consequently the absolute velocity of the exchange is practically independent of the hydrogen pressure or the exchange reaction is of zero order relative to the hydrogen pressure.

Figs. 3 and 4 show the progress of the hydrogenation and the exchange, respectively, under different pressures and on different catalysts. In each case the progress of the reaction corresponds to that shown in Figs. 1 and 2.

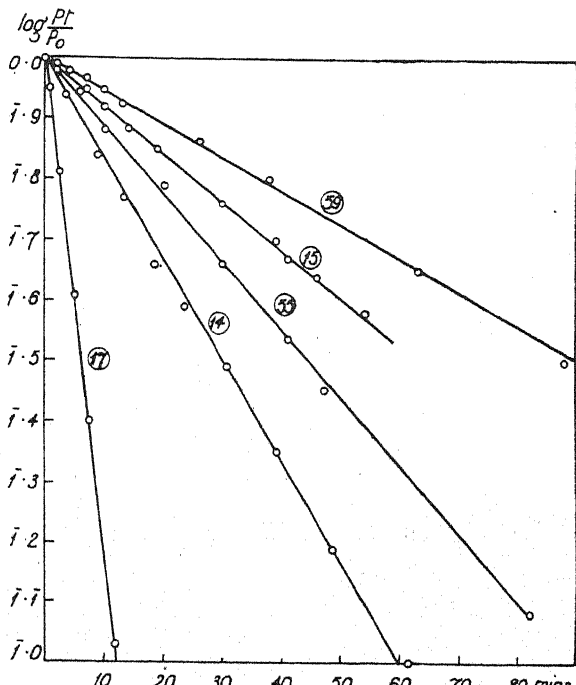


FIG. 3.—Progress of the Hydrogenation. Expt. No. 14: 50 mm. C_6H_6 + 36 mm. H_2 ; No. 55: 59 mm. C_6H_6 + 67 mm. D_2 ; No. 15: 52 mm., C_6H_6 + 55 mm. H_2 ; No. 59: 10 mm. C_6H_6 + 149 mm. H_2 , all at 17–18° C.; No. 17: 55 mm. C_6H_6 + 28 mm. H_2 at 96° C.

3. The Dependence of the Reaction Rate on Pressure.

From the progress of the hydrogenation reaction with time it is evident that the hydrogenation reaction is of the first order relative to the hydrogen pressure. (See Figs. 1 and 3). In Fig. 5 the progress of the hydrogenation is shown at different benzene pressures. It will be recognised that the reaction velocity is very little dependent on the benzene pressure, the respective half life periods being 61, 53, and 50 minutes at 3.5, 10, and 53 mm. of benzene respectively.

The dependence of the exchange reaction on the hydrogen pressure is evident from the progress of the exchange. The same result is obtained if the initial pressure of hydrogen is varied. For example: at 3 mm. benzene pressure and 15 mm. D_2 pressure the relative rate of the exchange reaction is exactly 5 times smaller than at 3 mm. D_2 (expts. No. 65–66).

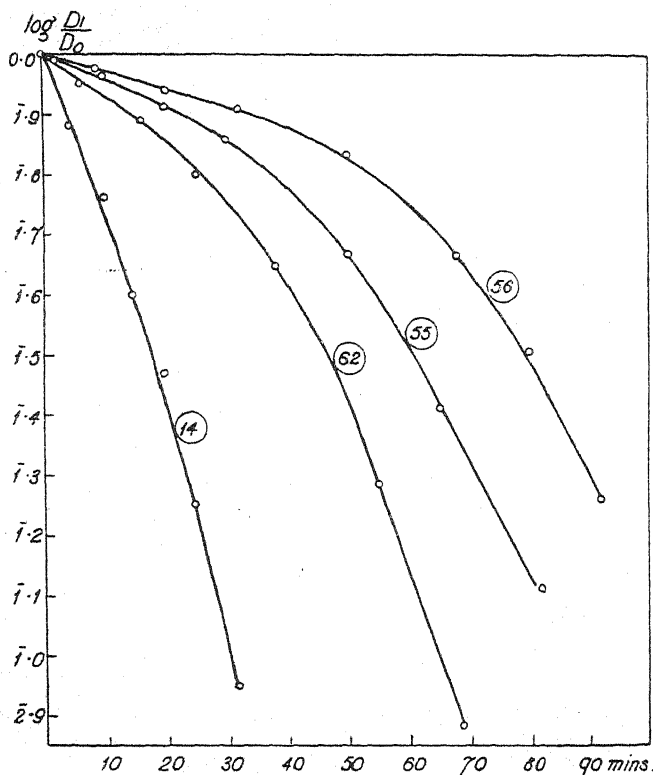


FIG. 4.—Progress of the Exchange. Expt. No 14: 50 mm. C_6H_6 + 36 mm., heavy hydrogen (40 per cent. D); No. 62: 48 mm. C_6H_6 + 44 mm. D_2 ; No. 55: 59 mm. C_6H_6 + 67 mm. D_2 ; No. 56: 60 mm. C_6H_6 + 100 mm. D_2 , all at $17-18^\circ C$.

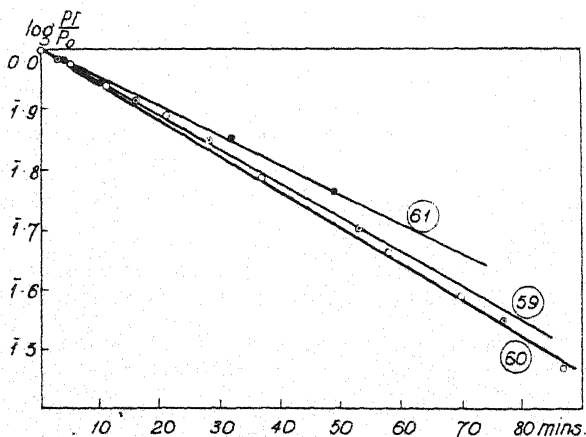


FIG. 5.—Progress of the Hydrogenation at different Benzene-pressures. Expt. No. 60: 53 mm. C_6H_6 + 129 mm. H_2 ; No. 59: 10 mm. C_6H_6 + 135 mm. H_2 ; No. 61: 3 mm. C_6H_6 + 121 mm. H_2 . All at $18^\circ C$.

The dependence of the exchange reaction on the benzene pressure is shown in Table II., the half life times being calculated from the initial velocity.

TABLE II.

No.	Benzene, mm.	Heavy Hydrogen, mm.	Half Life ($\tau = \frac{\ln 2}{k}$) in mins.
23	27	27	41
25	54	26	32
64	50	16	18
65	3	15	54

From the above mentioned data, one has to conclude that (1) the absolute rate of the exchange reaction is independent of the hydrogen pressure and proportional approximately to 0.4th power of the benzene pressure, and (2) the absolute rate of the hydrogenation reaction proportional to the hydrogen pressure is practically independent of the benzene pressure.

4. Dependence of the Reaction Rate on Temperature.

The dependence of both the hydrogenation and exchange reaction was investigated in some experiments from which a few examples are given in Table III.

TABLE III.

No.	Temp. °C.	Benzene, mm.	Hydrogen, mm.	Half Life Time in mins.	
				Hydrogenation.	Exchange.
15	17	52	30	38	—
16	96	52	30	3.5	—
22	17	26	25	—	35
21	96	26	23	—	1.1

The apparent heat of activation is 7 K. cal. and 9 K. cal. for the hydrogenation and exchange reaction respectively.

It will be recognised that the exchange reaction is somewhat more dependent on temperature than the hydrogenation.

5. Comparison of Reaction Rates.

The reaction rates of the hydrogenation and exchange in the gaseous phase have been compared :

- with each other ;
- with the conversion of *para*-hydrogen ;
- with the corresponding catalytic reactions in the liquid phase.

From the above mentioned data it will be evident that the relative rates of the hydrogenation and exchange reactions will depend on the pressure according to

$$\frac{\text{hydrogenation}}{\text{exchange}} \propto \frac{P_{H_2}}{P_{C_6H_6}^{0.4}} \quad (1)$$

In Table IV. the rates of hydrogenation and exchange are listed on different catalysts and different pressures at 17-18° C. The ratio exchange : hydrogenation is the larger the less hydrogen and the more benzene is present.

If one allows for the different dependence of hydrogenation and the exchange on the concentration of the reactants and reduces all data for the same partial pressure of hydrogen and benzene (say 1 mm. H_2 and 1 mm. C_6H_6), according to the formula (1) the ratio exchange hydrogenation so obtained does not vary very much on catalysts of different activity (Column 7, Table IV.).

The *para*-conversion was measured in order to obtain some information about the concentration of hydrogen on the surface of the catalyst. It

TABLE IV.

No.	Benzene. mm.	Hydrogen. mm.	Half Life Time in mins.		Exchange Hydrogenation	Exchange Hydrogen at 1 mm. H ₂ and 1 mm. C ₆ H ₆ .
			Hydrogenation.	Exchange.		
63	4	15.5	44	44	1.00	0.091
222	26	23	50	35	1.43	0.091
23	26	27	63	50	1.26	0.095
64	50	16	28	15	1.86	0.062
13	47	16	15	4	3.75	0.125
7	47	24	70	35	2.00	0.102
25	54	26	45	30	1.50	0.081
10	49	27	33	30	1.10	0.062
1	50	35	20	15	1.13	0.097
62	48	44	36	44	0.82	0.075
55	59	64	30	76	0.393	0.055
56	60	100	33	150	0.22	0.044

was found in the gaseous phase the *para*-conversion proceeded at least 100 times more quickly than either the hydrogenation or the exchange reaction. This is in contrast to the results obtained in the investigation of the catalytic exchange of hydrogen atoms with water or alcohol vapour, when it

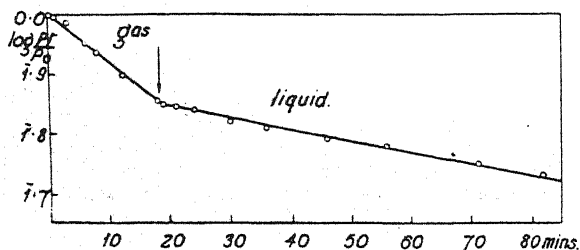


FIG. 6.—Progress of the Hydrogenation in the Gaseous and in the Liquid Phase.

was found that exchange and *para*-conversion proceeded approximately at the same speed.

The rate of hydrogenation and exchange in the gaseous phase was compared with that in the liquid either in subsequent runs or in the same experiments by bringing

the liquid benzene in contact with the catalyst. In the experiments with the liquid, the reaction was shaken with a speed of about 400 per minute, and the manometer was attached to the reaction vessel by a rubber tube.

The different rates of hydrogenation in the vapour and liquid phase are illustrated in Fig. 6, Expts. Nos. 78 and 79.

The initial pressure (P_0) of the hydrogen was 107 mm., and the pressure of benzene, 60 mm. The temperature of the catalyst was 17° C. In the eighteenth minute the catalyst was brought into contact with liquid benzene. In the figure, $\log P/P_0$ is plotted against time. It will be recognised that the progress of the hydrogenation and consequently its dependence on the hydrogen pressure obeys the same rule in the liquid phase as in the gaseous phase.

TABLE V.

No.	Hydrogen, mm.	Benzene, mm.	Half Life Time in mins.		Conversion.
			Hydrogenation.	Exchange.	
80	120	55	130	61	—
81	30	55	—	63	—
82	30	57	—	—	60

The half life times for the hydrogenation are 37.5 and 155 minutes for the gaseous and liquid phases respectively.

The relative rates of hydrogenation, exchange and *para*-conversion in the liquid are summarised in Table V.

From this table two important differences emerge compared with the reaction in the gaseous phase: (1) The half life time of the exchange in the liquid phase is independent of the hydrogen pressure, *i.e.*, the order of the exchange reaction relative to the pressure of hydrogen is unity, and not zero, as in the gas reaction: (2) In the liquid phase the conversion of *para*-hydrogen proceeds with the same speed as the exchange reaction.

6. Discussion.

In a previous paper,³ it was shown how it is possible to draw conclusions from the inhibition of the catalytic conversion of *para*-hydrogen by a certain substance with regard to its adsorbability. In the case of water, and the alcohols a strong inhibition of the conversion was found, showing that these substances are strongly adsorbed on platinised platinum and cover a great part of the catalyst. The dependence of the exchange reaction between heavy hydrogen and water or the alcohols on the pressure of water or alcohol vapour also indicates that water and alcohol are strongly adsorbed.

With benzene, however, no appreciable inhibition of the *para*-hydrogen conversion was found and it was concluded that only a small amount of benzene is adsorbed on platinised platinum. A similar behaviour was found also for acetone and ethylether.

The same results for benzene were obtained in the present paper as far as the conversion of *para*-hydrogen is concerned. On the other hand, from the dependence of the rate of exchange on the benzene pressure (Table II.) it appears that the adsorption layer is nearly saturated with benzene, the order of the exchange reaction being 0.4 with regard to benzene. The dependence of the hydrogenation on the benzene pressure even indicates complete saturation, the order of this reaction being zero with respect to benzene (Fig. 5).

At first sight these two conclusions—weak adsorption deduced from observation of the *para* conversion being not inhibited and strong adsorption deduced from the kinetics of the exchange and hydrogenation reactions—seem to be contradictory. This behaviour becomes, however, understandable if we consider it as an indication that benzene is not adsorbed on the same places of the catalyst as hydrogen. Thus, in this respect, benzene is adsorbed in a manner distinctly different from that of water, alcohol, or ethylene, which can all occupy the same places as hydrogen.*

Two explanations of this behaviour may be given: (a) the number of the groups active in adsorption is one for the alcohols, water, or ethylene (hydroxyl group or double bond), but three for benzene: or (b) the shape and dimension of the benzene molecule are different from those of the other molecules. The former explanation accords with a theory put forward by Balandin,⁷ who assumes that on metallic catalysts the benzene is adsorbed in a flat position and is held by the co-operation

* Kubota and Yoshikawa⁶ postulate three different places on a nickel catalyst on which ethylene, benzene and nitro-compounds, respectively, react with hydrogen, and which can be poisoned by ethyl sulphide, thiophene, and hydrogen sulphide, respectively.

⁶ B. Kubota and K. Yoshikawa, *Sci. Papers Inst. P.C.R.*, 1926, 3, 223.

⁷ A. A. Balandin, *Z. physik. Chemie, B*, 1929, 2, 289.

of three atoms of the catalysts arranged in an equilateral triangle of given dimension. According to this view, on a catalyst consisting of, say, hexahedral and octahedral planes, benzene is adsorbed only on the octahedral ones, whereas hydrogen could be adsorbed by both kinds of planes.

According to Schmidt,⁸ however, the accessibility to the catalyst is determined decisively by the shape and dimensions of the molecules in question, since in his view, the reaction takes place in the interior of the catalyst. The larger and the more complicated the structure of the molecule, the less chance it has to enter the interior of the catalyst to be adsorbed and undergo a chemical reaction there. In our opinion, however, Schmidt's view is not yet proved exactly. Moreover, according to Schmidt's view, in the present case one would expect the benzene to close up the fine canals leading to the interior of the catalyst. Thus, contrary to actual observation, the conversion of *para*-hydrogen should be inhibited by this effect, although no actual displacement of hydrogen by benzene would happen.

Consequently we should favour the view put forward by Balandin as an explanation for hydrogen and benzene being adsorbed on distinctly different places of the platinum catalyst. Furthermore, the fact that the conversion of *para*-hydrogen is not appreciably inhibited even at a relatively high pressure of benzene (saturation pressure at the temperature of the catalyst) shows that there are only a few places which adsorb benzene, compared with those that adsorb hydrogen. These places, however, hold the benzene strongly adsorbed.

We now consider the connection between the exchange reaction and the hydrogenation proposed by Horiuti and Polanyi.⁴ According to these authors, the first step in the hydrogenation is the addition of one hydrogen atom which leads to the formation of the "half hydrogenated state." The half hydrogenated state can either lose one hydrogen atom or take up a second one, thus leading either to exchange or hydrogenation.

According to this scheme, the hydrogenation (A) and exchange (E) should depend upon concentration of benzene and of hydrogen in the adsorption layer as given by *

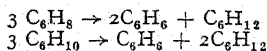
$$A \propto [C_6H_6][H]^2 \quad . \quad . \quad . \quad . \quad (2)$$

$$E \propto [C_6H_6][H] \quad . \quad . \quad . \quad . \quad (3)$$

These formulae, however, do not agree with the experimental results. Firstly, the dependence of the hydrogenation and exchange on the concentration of the benzene is not the same, since the exchange varies

⁸ O. Schmidt, *Chem. Rev.*, 1933, **12**, 363; *Z. physik. Chemie, A*, 1933, **165**, 139.

* In this discussion we have assumed that the hydrogenation of benzene proceeds in consecutive steps through di-hydro-benzene and cyclo-hexene, and not by simultaneous addition of three hydrogen molecules, as is postulated by Balandin.⁷ A failure to detect these intermediate products in the hydrogenation of benzene might be explained by a higher reactivity of these intermediates⁹ and the establishment of equilibria¹⁰ such as



owing to their higher affinity to hydrogen. Cf. also Hückel.¹¹

⁹ R. Truffaut, *Bull. Soc. Chimie France*, 1934, [5], **1**, 206.

¹⁰ N. Zelinsky, *Ber.*, 1925, **58**, 185.

¹¹ W. Hückel, *Theoretische Grundlagen der organischen Chemie*, 1934, Vol. I.,

as the 0.4th power of the benzene pressure, whereas the hydrogenation is practically independent of the benzene pressure. Still larger, however, is the discrepancy in the dependence of the reaction rates on the hydrogen pressure. The exchange reaction proved to be of zero order with regard to hydrogen. If this is to be explained by an adsorption layer completely saturated with hydrogen, one also should expect the hydrogenation to be of zero order with regard to hydrogen. In fact, however, the hydrogenation is of the first order.

Thus, on the basis of the kinetic measurements, we have to conclude that in the gaseous phase there is no direct connection between hydrogen and exchange as postulated by Horiuti and Polanyi. In a forthcoming paper we shall show, furthermore, that the picture of the hydrogenation as an independent approach of two hydrogen atoms is incorrect. Rather, the hydrogenation is a simultaneous addition of the two hydrogen atoms of one catalytically activated hydrogen molecule, as already pointed out.¹ A similar view was considered by Vavon¹² in some special cases.

For the exchange reaction we would again propose the dissociation mechanism, according to which the adsorbed benzene molecules lose one hydrogen atom and take up another (heavy) hydrogen atom.

For an understanding of the dependence of the hydrogenation and exchange reactions on the pressure, the hydrogenation and exchange must be considered as directed against different points of the benzene molecules. If we visualise the adsorption of benzene to occur according to the picture proposed by Balandin (see Fig. 7) and assume that the hydrogen is adsorbed, for example, in the middle of the triangles, we can expect that though hydrogen covers practically all of the catalyst, the adsorption of hydrogen at places active in the addition of hydrogen (marked with crosses) will be relatively weak, owing to a displacement effect. This is the cause of the observed order (unity) of the hydrogenation reaction relative to hydrogen.

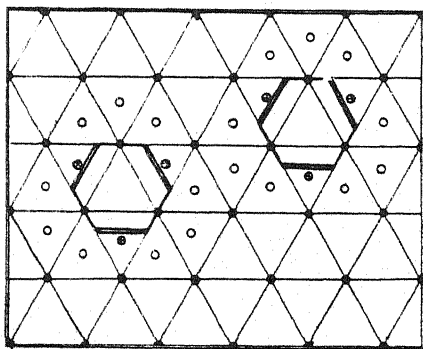


FIG. 7.

On the other hand, the rate determining step in the exchange reaction is the rupture of the bond between one hydrogen atom and the nucleus in the benzene molecules, since in the neighbourhood of such a point relatively large amounts of hydrogen will be adsorbed.

The different dependence of the hydrogenation and exchange reaction on the concentration of benzene is probably due to the fact that, at places of the catalyst which are active in the rupture of the C-H bond, benzene is adsorbed slightly less strongly than at places which do not cause any dissociation. This would account for the slight dependence on the benzene pressure.

Finally, we consider interaction in the liquid phase. The simplest

¹² G. Vavon, *Bull. Soc. Chimie France*, 1927, [4], 41, 1253.

explanation for the strong inhibition of the *ortho-para*-hydrogen conversion in the liquid was suggested in a previous paper:³ when a catalyst is in contact with liquid benzene, most of its surface is covered by a film of benzene and but little hydrogen is present in the adsorption layer. It might appear rather strange that the amount of hydrogen present in the adsorption layer should be different on a catalyst whether in contact with benzene vapour of saturation pressure or with liquid benzene. The condensation of the vapour to liquid takes place on a solid only at pressures higher than the saturation pressure if the solid is not wetted by the liquid.¹³ Bismuth is not wetted by benzene and therefore the composition of the adsorption layer is different when the platinum is in contact with vapour or liquid. In the latter case a liquid film can be formed which will displace the hydrogen.

Since the concentration of hydrogen on the catalyst is small, the rupture of the C-H bond is no longer the rate determining step in the exchange reaction, but the supply of D-atoms to the C_6H_5 -radicals. In the previous paper it was shown that the velocity of exchange is proportional to the amount of D_2 adsorbed, if the reaction partner replaces hydrogen in the adsorption layer. This explains why the order of hydrogenation with regard to hydrogen is unity, in contrast to zero in the gaseous reaction. This is the state of affairs if there is only a monomolecular layer of benzene on the catalyst. If, however, the shaking or stirring is not efficient enough, there can be a relatively thick layer of benzene on the catalyst and the rate of the reaction is governed by diffusion processes. Obviously, between these two extremes cases, any intermediate state might occur. A detailed study of the rôle of stationary liquid films in the catalytic interaction of benzene and hydrogen is, however, outside the scope of the present paper. At the moment we cannot decide with certainty whether the observed rates of reaction characterise the true reactions or diffusion processes.

Summary.

The catalytic interaction of heavy hydrogen and benzene has been investigated on a platinised platinum foil at room temperatures and at different partial pressures of benzene and hydrogen ranging from 3 to 150 mm. Hg. It was found that two reactions occur: (a) exchange of hydrogen atoms between benzene and gaseous hydrogen, (b) hydrogenation of benzene. These two reactions are independent of each other. In the gaseous phase the absolute rate of the exchange is independent of the hydrogen pressure and proportional to approximately the 0.4th power of the benzene pressure, and the absolute rate of the hydrogenation is proportional to the hydrogen pressure and practically independent of the benzene pressure. The rate of exchange and hydrogenation has been compared with each other in the gaseous and liquid phase and with the speed of the conversion of *para*-hydrogen, the catalyst being in contact with gaseous and liquid benzene. In the gaseous phase the conversion proceeds very much faster than the exchange, whereas in the liquid phase its rate is about the same as that of the exchange. The rates of hydrogenation and exchange are somewhat smaller in the liquid phase than in the gaseous phase. These results lead to the following conclusions:

(a) In the gaseous phase the surface of the catalyst is mainly covered with hydrogen and the benzene molecules occupy only a certain few places which absorb them very strongly.

¹³ Cf. Freundlich, *Kapillarchemie*, vol. I., 1930, p. 234.

(b) In the liquid phase the catalyst is covered with a film of benzene which displaces hydrogen.

(c) The hydrogenation and exchange proceed according to two distinctly different mechanisms: the hydrogenation involves a simultaneous addition of two hydrogen atoms, whereas the exchange consists of the dissociation of the benzene molecules into a phenyl-radical and a hydrogen atom followed by the reunion of the phenyl-radical with another (heavy) hydrogen atom present in the adsorption layer.

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THE MECHANISM OF HYDROGENATION REACTIONS AND THE FORMATION OF STEREO-CHEMICAL ISOMERS.

BY A. FARKAS AND L. FARKAS.

(Received 19th April, 1937.)

In a previous paper it was shown that under certain conditions the catalytic hydrogenation of ethylene is accompanied by an exchange of hydrogen atoms between ethylene and gaseous hydrogen.¹ This reaction becomes evident if heavy hydrogen is used instead of ordinary hydrogen. Further investigation² showed that the exchange reaction may accompany other hydrogenation reactions also, and that these two reactions proceed according to the following two different and independent mechanisms³:—

(1) The catalytic* hydrogenation consists of the simultaneous addition of the two atoms of the same hydrogen molecule adsorbed on the surface of the catalyst. Thus it does not involve the consecutive addition of two independent hydrogen atoms to the unsaturated compound.

(2) The catalytic exchange reaction involves the rupture of a C—H bond in the unsaturated compound and the subsequent reunion of the so formed radical with another (heavy) hydrogen atom formed by the dissociation of a (heavy) hydrogen molecule.¹²

Another type of isotopic exchange is involved in the interaction of heavy hydrogen and acetone (see below).

It is evident that these two reactions must have a decisive rôle in the formation and interconversion of stereochemical isomers. A review of the literature has shown that other investigators, especially Bourguet⁴ and Vavon⁵ have already suggested views closely related to the above-

¹ A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc., A*, 1934, **146**, 630.

² J. Horiuti, G. Ogden and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 663.

³ A. Farkas and L. Farkas, *ibid.*, 1937, **33**, 827.

⁴ We shall use "catalytic" in the sense "catalysed by metals."

⁵ M. Bourguet, *Bull. Soc. Chim. France*, 1932, **4**, **51**, 253.

⁶ G. Vavon, *ibid.*, 1927, **4**, **41**, 1253.

mentioned mechanisms, but based on more indirect evidence. Their theory, however, has not yet been generally accepted.^{6, 7, 8}

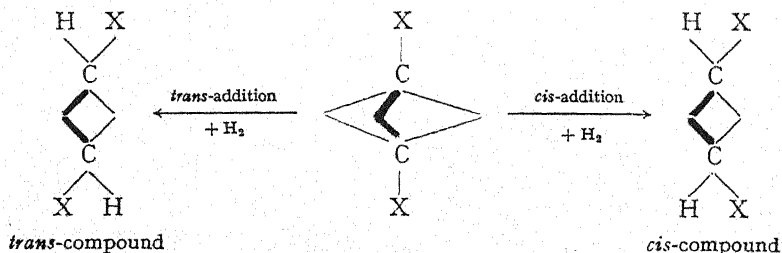
The purpose of the present paper is to review the literature on this subject in the light of recent experiments and to give an explanation for the formation of stereochemical isomers. Anticipating the results, it may be stated that, in the authors' opinion, it is possible to explain all relevant experimental results without any serious exception on the basis of the suggested mechanisms for the hydrogenation and exchange.

The mechanism for the catalytic hydrogenation follows from experiments on the catalytic interaction of *para*-hydrogen and ethylene.^{1, 9} In the absence of ethylene there was a rapid conversion of *para*-hydrogen on the surface of the catalyst (Ni or Pt) showing dissociation of the *para*-hydrogen molecule and subsequent recombination of the atom so formed. In the presence of ethylene, however, the conversion was strongly inhibited though hydrogenation was proceeding. These experiments prove directly that the hydrogen molecule is taken up by the ethylene on the surface of the catalyst, as soon as it comes into contact with the catalyst, before its atoms have any chance to evaporate again by recombining with each other or other atoms. The simplest explanation for such behaviour is that both atoms of the same molecule are taken up simultaneously by the ethylene.

A similar mechanism for the hydrogenation was suggested by Vavon⁵ based on the observations on the hydrogenation of conjugated double bonds by hydrogen activated catalytically (by metals) and by hydrogen in the nascent state. Hydrogen in the nascent state is easily added in 1-4 position. In catalytic hydrogenation, however, 1-4 addition is generally not obtained but each double bond is hydrogenated separately. Vavon explains this by assuming that hydrogen in the nascent state consists of atoms which can attack the conjugated bonds independently, whereas the catalytically activated hydrogen consists of deformed molecules, which are added as such to each of the double bonds. Bourguet⁴ is of the same view regarding the mechanism of the catalytic hydrogenation and concludes that the addition of hydrogen to treble bonds in acetylene compounds should lead to the formation of the corresponding *cis* compounds. He also pointed out the possibility of subsequent *cis-trans* conversion being induced by the hydrogenation catalyst (see below).

We will consider the following cases of addition reactions :

(a) Addition to a Treble Bond.



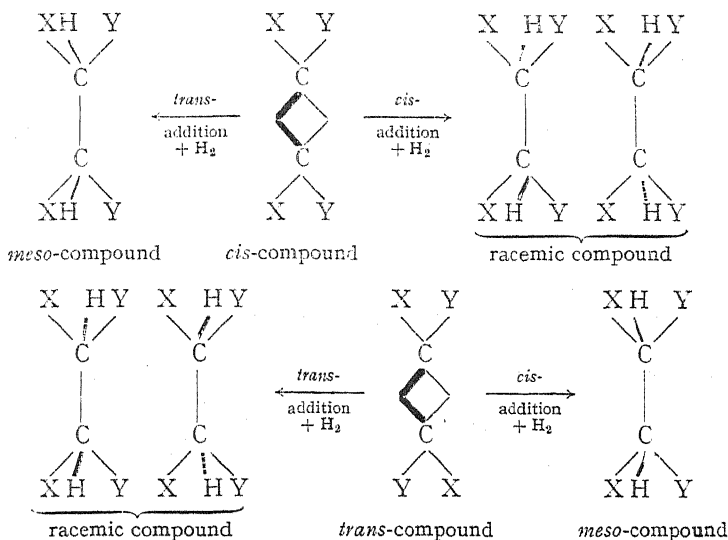
⁶ W. Hückel, *Theoretische Grundlagen der organischen Chemie*, 1935, 321.

⁷ K. Freudenberg, *Stereochemie*, 1933, 523.

⁸ S. Goldschmidt, *Stereochemie, Handbuch der chemischen Physik*, 1933, 100.

⁹ A. Farkas and L. Farkas (*unpublished results*).

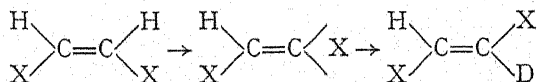
(b) Addition to a Double Bond.



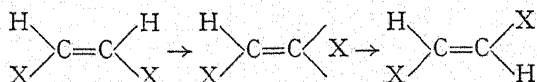
In reviewing the experimental data concerning these addition reactions we have to bear in mind that though the course of the reaction may be determined by stereo-chemical influences, its ultimate aim is the attainment of the thermodynamical equilibrium, *i.e.*, the formation of the stable compound (or compounds) among all the possible isomers. The thermodynamically stable equilibrium can be reached either in a direct reaction, if the addition proceeds over independent atoms or through conversion reactions of the particular isomers formed by the addition of whole molecules. It has already been shown that such conversion reactions between stereo-isomers exist and that they proceed not only under the influence of alkalis, acids, halogens, etc., but also on catalysts as used in the hydrogenation.^{10, 10a} The recent experiments on the exchange reaction give more direct evidence for the mechanism of such conversions.

The mechanism of the catalytic exchange of hydrogen atoms in the ethylene molecules will cause a *cis-trans* conversion according to the following scheme:¹¹

Exchange and *cis-trans* conversion:



cis-trans conversion:



¹⁰ R. Kuhn in Freudenberg's *Stereochemie*, 1933, 913.

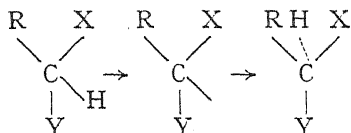
^{10a} Lowe and Ase, *Chem. Zentralblatt*, 1906, II., 492.

¹¹ For another mechanism cf. J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, 30, 1164.

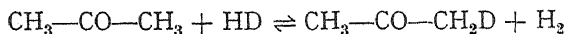
Since we know that this type of exchange is operative very much more easily with ethylenic (or aromatic) compounds than with saturated compounds according to



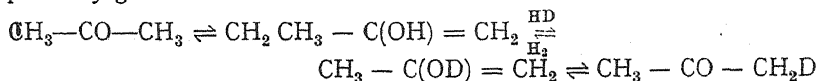
we should not expect a racemisation to happen according to



so easily as the *cis-trans* isomeration through the corresponding dissociation mechanism. But there is another type of catalytic intramolecular racemisation which is closely related to the catalytic exchange of hydrogen atoms between acetone and gaseous hydrogen.¹² This exchange

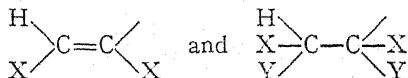


probably goes over an enolisation



on the surface of the catalyst, since from experiments on the catalytic exchange of hydrogen atoms between alcohols and gaseous hydrogen we know that the hydrogen atom in the hydroxyl group is readily exchanged.¹² We should expect a similar exchange reaction to occur with other compounds containing a CO-group like acids, esters or aldehydes. This type of enolisation will cause a racemisation of optically active carboxylic acids on the surface of the catalyst. In the catalytic hydrogenation experiments, maleic and fumaric acid derivatives have mostly been used, in which the "racemisation" in fact means the formation of the *meso*-compound from the mixture of the optically active isomers,¹³ the *meso*-compounds being usually the stable ones (*cf.* below).

In the following we shall assume that according to the proposed mechanism of catalytic hydrogenation the atoms of the hydrogen molecule are added always primarily in *cis*-position and that in the hydrogenation with nascent hydrogen two independent atoms are added in consecutive steps and the thermodynamically stable compound is formed.¹⁴ In our view the thermodynamical equilibrium is established since the intermediate compounds



formed by the addition of the first hydrogen atom to the unsaturated compounds are capable of adjusting the substituents in a position of minimum potential energy. A similar adjustment occurs in excited electronic levels of ethylene derivatives and of optically active compounds

¹² A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1937, **33**, 678.

¹³ This mechanism is analogous to the mechanism of the homogeneous racemisation in solutions under the influence of alkali, *cf.* Freudenberg, *Stereochemie* (1933) 858.

¹⁴ For a special mechanism for the hydrogenation with nascent hydrogen, *cf.* Burton and Ingold (Burton and Ingold, *J. Chem. Soc.*, 1929, 2022).

in the *cis-trans* conversion and racemisation, respectively, under the influence of light.¹⁵

Since usually the *trans*-ethylene derivatives and the *meso*-forms are the stable compounds¹⁶ we obtain the following schemes for the hydrogenation:

The acetylene derivatives listed in Table I. react with hydrogen strictly according to Scheme 1 yielding *cis*-compounds in the catalytic hydrogenation and *trans*-compounds in the reaction with nascent hydrogen.

The only exception is acetylene-dicarboxylic acid. In the catalytic hydrogenation of this substance Bourguel¹⁸ finds quantitative formation of the *cis*-compound but Ott and Schröter¹⁷ obtain increasing amounts of the *trans*-compound as the time of reaction increases. We should suggest that this is due to the same type of exchange reaction as described for ethylene which manifests

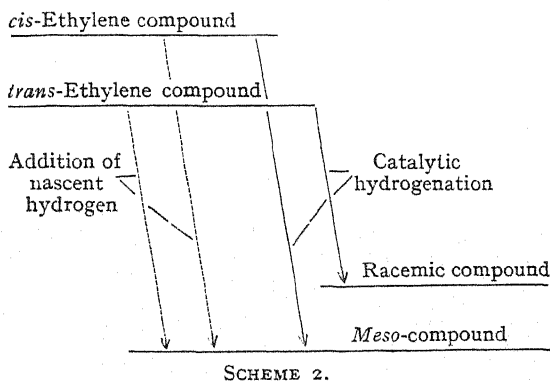
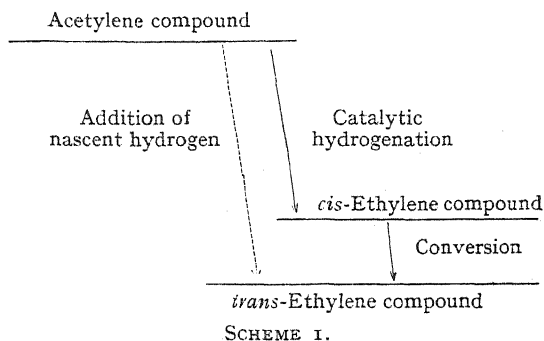
itself in this case as *cis-trans* conversion of the primarily formed maleic acid.

According to Scheme 2, in the catalytic hydrogenation of ethylene compounds, we have to expect from *cis*-compounds the *meso*-compounds and from *trans*-compounds the racemic compounds. The addition of nascent hydrogen should give in both cases, however, the same thermodynamically stable, *i.e.*, the *meso*- or racemic form, as the case may be.

The catalytic hydrogenation¹⁹ of the following compounds proceeds in agreement with this scheme:

Dimethyl-maleic acid \rightarrow *meso*-form
 Dimethyl-fumaric acid \rightarrow racemic form
cis-Dimethyl-stilbene \rightarrow *meso*-form
trans-Dimethyl-stilbene \rightarrow racemic form.

The apparent exceptions from Scheme 2 are as follows: According to Ott¹⁹ the catalytic hydrogenation of dimethyl-fumaric acid on palladium can yield up to 61 per cent. *meso*-compound and also in the addition



¹⁵ A. R. Olson, *Trans. Faraday Soc.*, 1931, **27**, 69; A. R. Olson and W. Maroney, *J. Am. Chem. Soc.*, 1934, **56**, 1320.

¹⁶ K. L. Wolf in *Leipziger Vorträge*, 1931, p. 17.

¹⁷ E. Ott and R. Schröter, *Ber.*, 1927, **60**, 624.

¹⁸ M. Bourguel, *Comptes rend.*, 1925, **180**, 1753.

¹⁹ E. Ott, *Ber.*, 1928, **61**, 2119, 2124.

TABLE I

Acetylene-compound.	Catalytic Hydrogenation gives <i>CIS</i> -compounds.	Addition of Nascent Hydrogen gives <i>TRANS</i> - compounds	Refer- ences.
Acetylene di-carboxylic acid $\text{HOOC}-\text{C}\equiv\text{C}-\text{COOH}$	Maleic acid $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$	—	(17, 18)
Tetrollic acid $\text{CH}_3-\text{C}\equiv\text{C}-\text{COOH}$	iso-Crotonic acid $\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$	—	(18), [19a]
Butine carboxylic acid $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{C}-\text{COOH}$	cis-Butene carboxylic acid $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{COOH}$	—	(20)
Pentene carboxylic acid $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{C}-\text{COOH}$	cis-Pentene carboxylic acid $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{COOH}$	—	(20)
Stearic acid $\text{CH}_3-[\text{CH}_2]_7-\text{C}\equiv\text{C}-[\text{CH}_2]_7-\text{COOH}$	Oleic acid $\text{CH}_3-[\text{CH}_2]_7-\text{CH}=\text{CH}-[\text{CH}_2]_7-\text{COOH}$	Elaidic acid	(21)
Behenic acid $\text{CH}_3-[\text{CH}_2]_9-\text{C}\equiv\text{C}-[\text{CH}_2]_{11}-\text{COOH}$	Erucic acid $\text{CH}_3-[\text{CH}_2]_9-\text{CH}=\text{CH}-[\text{CH}_2]_{11}-\text{COOH}$	Brassicic acid	(21)
Tetra-methyl-butene-diol $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{CH}_3)_2$	cis-Tetra-methyl-butene-diol $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}(\text{OH})(\text{CH}_3)_2$	trans-Tetra-methyl-butene-diol	(18, 22, 23)
Tolane $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$	iso-Stilbene $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$	Stilbene	(17, 20, 24, 25, 26)
Phenyl-propionic acid $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{COOH}$	iso-Cynamic acid $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{COOH}$	Cynamic acid	(18, 27, 28, 29, 30)
Phenylpropionic alcohol $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$	iso-Cynamic alcohol $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$	—	(20)

of nascent hydrogen 58 per cent. *meso*-compound can be formed besides 42 per cent. of the racemic isomers (*cf.* Fittig³¹). This latter observation is due to the fact that in the case of dimethyl-succinic acids a mixture of the racemic and *meso*-forms corresponds to an equilibrium and not the *meso*-form alone.^{16, 32} In the hydrogenation experiment with palladium, a conversion reaction involving catalytic enolisation was operative and responsible for the formation of an amount of the *meso*-form which practically corresponds to equilibrium. Similarly when *trans*-dimethylstilbene is hydrogenated with nascent hydrogen a mixture of the racemic and *meso*-forms is obtained. We again ascribe this to the position of the equilibrium between the isomers.

It is worth while to note that the addition of halogens to double bonds follows in general a similar course as the addition of nascent hydrogen, although according to Goldschmidt³³ there is no rule which governs the addition of halogens to *cis*- and *trans*-ethylene derivatives.

Berthoud³⁴ showed that in the photochemical bromination of ethylene-derivatives each bromine atom is added separately and primarily a mono-

^{19a} A. Gonzalez, *Chem. Zentr.*, 1925, I., 2547.

²⁰ M. Bourguet and J. Yvon, *Comptes rend.*, 1926, 182, 224.

²¹ Gonzalez, *Chem. Zentr.*, 1926, II, 183.

²² Salkind, *Ber.*, 1927, 56, 187.

²³ *Ibid.*, 60, 1125.

²⁴ Kelber and Schwarz, *Ber.*, 1913, 45, 1949.

²⁵ Strauss, *Lieb. Ann.*, 1905, 342, 201.

²⁶ Aronstein and Hollemann, *Ber.*, 1888, 21, 2833.

²⁷ Paal and Hartmann, *Ber.*, 1909, 42, 3931; Paal and Schwarz, *Ber.*, 1919, 48, 1202.

²⁸ G. Vavon and Manta, *Bull. Soc. Chim. France*, 1927, 4, 41, 140.

²⁹ Aronstein and Hollemann, *Ber.*, 1889, 22, 1881.

³⁰ E. Fischer, *Lieb. Ann.*, 1912, 386, 380.

³¹ R. Fittig, *ibid.*, 1899, 304, 178.

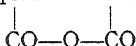
³² W. Basyrin, *Ber.*, 1913, 46, 3230.

³³ Goldschmidt in Freudenberg's *Stereochemie*, 1933, 519.

³⁴ A. Berthoud, *Helv. Chim. Acta*, 1930, 13, 385.

brom-ethylene compound is formed with a three-valent carbon atom. According to Berthoud³⁵ such a mechanism will be probably followed in other halogenation reactions which are not induced by light and there is a possibility of intermolecular rearrangement among the substituents in the intermediate compound owing to its unsaturated character. The second halogen atom will be added to the different forms of the intermediate compound in such a way that finally the stablest di-halogen compound is obtained. The same mechanism holds also for the halogenation of acetylene derivatives and for cases of halogenation involving ions.³⁶ This mechanism of the halogenation corresponds exactly to the proposed mechanism for the addition of nascent hydrogen. In fact, we find that all examples of halogenation so far investigated are in complete agreement with this scheme.

The chlorination or bromination of fumaric or maleic acid and of their salts yields always 80-100 per cent. stable *meso*-compound.^{37, 38} The same is true also for the addition of HOCl to maleic or fumaric acid.^{39, 40} The bromination and chlorination of maleic anhydride⁴¹⁻⁴³ is interesting; the racemic form is obtained (instead of the *meso*-form), in agreement with the observation that among of the isomers of the anhydrides of the type $R_1CH-CHR_2$ in general the racemic isomers are the stable ones.¹⁶



The above-mentioned experimental data strongly support the proposed mechanism for the catalytic hydrogenation and related phenomena. There are, however, a number of experiments which could be used for testing the present theory further.

Firstly the simultaneous addition of both atoms of the same hydrogen molecule can be tested by investigating the structure of the ethylene and ethane-derivatives formed from acetylene and ethylene derivatives, when the hydrogenation is carried out with a mixture of H_2 and D_2 . If the surface of the catalyst is completely covered with the unsaturated compound and there are no unoccupied places to bring about the formation of HD molecules from the mixture $H_2 + D_2$ one should obtain only the symmetric compounds $HXC = CYH$ and $DXC = CYD$ and $HXYC - CYXH$ and $DXYC - CYXD$. Substituted compounds which do not contain CO - groups are especially suitable for such an investigation, as this avoids any complication due to exchange of hydrogen atoms between the gaseous hydrogen and the reaction partner. The structure of the resulting compound will be revealed by analysis of their infra-red or Raman Spectra.

Since the equilibrium between isomers of some substituted dicarboxylic acids of the type $R_1CH(COOH) - HC(COOH)R_2$ is known, one could test whether the hydrogenation of the corresponding *cis* and *trans* ethylene dicarboxylic acids $R_1C(COOH) = C(COOH)R_2$ with nascent hydrogen will proceed according to the mechanism proposed in this paper, *i.e.*, will give the *meso*-(mesoid) form alone or together with the racemic form depending on the position of the above-mentioned equilibrium.

A comparison of the hydrogenation of these acids with that of the corresponding anhydrides should be interesting since in most cases the equilibrium between the isomers of the hydrogenated anhydrides is distinctly different from that of the corresponding acids.¹⁶ So in cases in which the hydrogenation of acids with nascent hydrogen would give, say,

³⁵ A. Berthoud, *Chem. Zentr.*, 1933, 1, 2931.

³⁶ P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, 1936, 58, 466.

³⁷ R. Kuhn and Wagner-Jauregg, *Ber.*, 1928, 61, 520.

³⁸ Terry and Eichelberger, *J. Am. Chem. Soc.*, 1925, 47, 1067 and 1462.

³⁹ W. Kuhn, *Ber.*, 1925, 58, 919.

⁴⁰ Lossen, *Lieb. Ann.*, 1906, 348, 273.

⁴¹ B. Holmberg, *J. prakt. Chemie*, 1911, 2, 84, 145.

⁴² A. Michael, *ibid.*, 1895, 52, 293.

⁴³ Pictet, *Ber.*, 1880, 13, 1670.

the stable *meso*-form, we should expect in that of the anhydrides the racemic form and *vice versa*.

In the hydrogenation of *trans*-ethylene derivatives which do not contain CO— groups, and thus are not liable to enolisation, we should expect the formation of the stable *meso* or mesoid compounds if nascent hydrogen is used and the racemic form if the hydrogen is activated catalytically.

Finally, we want to draw attention to a possible comparison of the rates of the catalytic *cis-trans* conversion and racemic-*meso* conversion with the rate of the exchange reaction involving heavy hydrogen. Such an investigation is planned in this laboratory.

Summary.

It is suggested that in the catalytic hydrogenation of unsaturated compounds both hydrogen atoms of the same hydrogen molecule are added simultaneously in contrast to the addition of nascent hydrogen which involves the consecutive addition of two independent atoms. It is shown that according to these mechanisms the catalytic hydrogenation of acetylene compounds, of *cis*- and of *trans*-ethylene derivatives should lead to *cis*-ethylene compounds, *meso*- (mesoid) and racemic compounds respectively and the addition of nascent hydrogen to the thermodynamically stable stereo-isomers. The stable isomers are usually the *trans*-ethylene compounds and the *meso*-compounds. A review of the literature shows complete agreement with these mechanisms of hydrogenation. Apparent exceptions can be accounted for by a catalytic conversion of the primarily formed unstable compounds into the thermodynamically stable ones. From experiments on the catalytic exchange of hydrogen atoms between gaseous hydrogen and organic compounds it is shown that such catalytic conversion reactions only occur with disubstituted ethylene derivatives and compounds containing CO groups. It is pointed out that there is a close similarity between halogenation reactions and the addition of nascent hydrogen as far as the formation of the stereo-isomers is concerned.

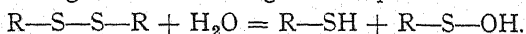
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THE ACTION OF LIGHT ON WOOL. PART I. THE TITRATION CURVES OF INTACT AND EXPOSED WOOLS.

By P. R. McMAHON AND J. B. SPEAKMAN.

Received 29th April, 1937.

The disulphide bonds of strained animal fibres are readily hydrolysed by steam or boiling water¹ according to the equation:—

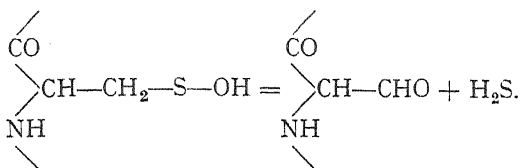


Decomposition of a similar character takes place in caustic soda solution in the cold,² even with unstrained fibres, but the sulphenic acid decom-

¹ Speakman, *Nature*, 1933, **132**, 930.

² Schöberl, *Annalen*, 1933, **507**, 111; *Collegium*, 1936, 412. Harris, *Bureau of Standards J. of Research*, 1936, **16**, 475.

poses and, apart from side reactions,³ half the sulphur from each hydrolysed disulphide bond is lost as hydrogen sulphide :—



Although the disulphide bonds of unstrained fibres are attacked by water at temperatures as low as 55° C., with liberation of volatile sulphur compounds, no significant hydrolysis takes place at temperatures below 45° C.⁴ There is, however, much evidence to show that when animal fibres are exposed to light and air, the disulphide bonds are rapidly hydrolysed at ordinary temperatures. For example, Kertesz,⁵ von Bergen⁶ and Sommer,⁷ found that sulphuric acid is formed when wool is irradiated, sulphur dioxide being recognised as a precursor of sulphuric acid by both Meunier and Rey⁸ and King.⁹ Since hydrogen sulphide is readily oxidised under the influence of light, it seems probable that the disulphide bonds of animal fibres undergo the same changes on exposure to light and air as in caustic soda solution. This deduction, which is in agreement with the work of Schöberl¹⁰ and Harris,¹¹ is of considerable importance because wool fibres are inevitably exposed to light and air during growth, the length of the affected tip section varying inversely with the density of the fleece, besides being dependent on the position of the fibres on the animal. The existence of such damage in fleece wool was recognised by von Bergen,⁶ but its extent is best illustrated by the following data for the sulphur contents of tip, middle and root sections of staples of New Zealand Romney wool.⁴ The staples were taken from a single animal, part of whose fleece had been fitted with a fabric cover; whereas the britch and neck wools were freely exposed to light during the whole period of growth, that from the side was protected by the cover.

TABLE I.

Section.	Sulphur Content (Per Cent. on Dry Wt.) of:		
	Britch (Uncovered).	Neck (Uncovered).	Side (Covered).
Tip . . .	2.78	2.83	3.27
Middle . .	3.26	3.18	3.23
Root . . .	3.45	3.55	3.53

Thus about 14 per cent. of the total sulphur in the tip wool is lost when the fibres are exposed to light during growth or, if it is assumed that the sulphur is lost as hydrogen sulphide according to the mechanism outlined above, about 28 per cent. of the disulphide bonds in the exposed tip section of the wool are hydrolysed under the influence of light.

³ Speakman and Whewell, *J. Soc. Dyers and Colourists*, 1936, **52**, 380.

⁴ Speakman, *J. Text. Inst.*, 1936, **27**, 231.

⁵ Kertesz, *Z. angew. Chem.*, 1919, **32** (1), 168.

⁶ von Bergen, *Mell. Textilber.*, 1923, **4**, 23; 1925, **6**, 745; 1926, **7**, 451.

⁷ Sommer, *Leip. Monats. f. Textilind.*, 1927, **42**, 35, 96, 158, 206.

⁸ Meunier and Rey, *Comptes Rendus*, 1926, **183**, 596.

⁹ King, *J. Soc. Dyers and Colourists*, 1928, **44**, 14, 233.

¹⁰ Schöberl, *Naturwiss.*, 1935, **23**, 391.

¹¹ Harris, *Bureau of Standards J. of Research*, 1936, **17**, 97.

It is to be expected, therefore, that raw wool fibres will contain a considerable, but arbitrary, number of sulphhydryl groups, which cannot fail to affect the alkali-titration curve. Should this be the case, the previously published titration curve of Cotswold wool¹² would have no general validity, and the characteristic step at p_H 10 would be due to combination of alkali with sulphhydryl groups, rather than to the suggested back-titration of lysine side chains in salt linkages. With such considerations in mind, it was decided to determine the titration curve of intact wool, comprising the unexposed root ends of a number of staples. In addition, however, the titration curve of the exposed tip sections of the same staples was also determined in order, by comparison with the curve for intact wool, to obtain further information concerning the changes taking place when fibres are exposed to the action of light and air.

Experimental.

New Zealand Romney wool was selected as being particularly suitable for use in the following experiments because, although staples taken from

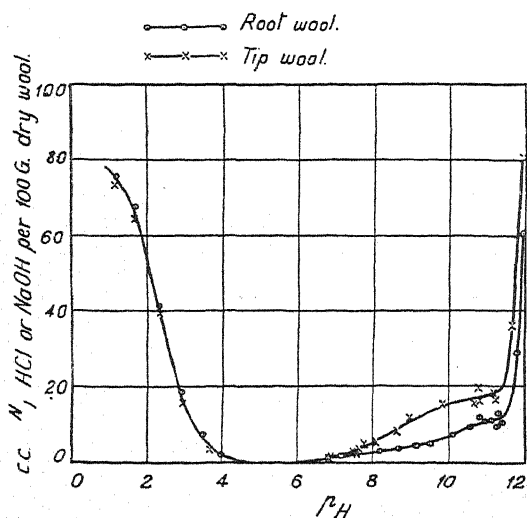


FIG. 1.

80 g. and 100 g. of air-dry tip and root wool, respectively, were obtained. The two lots of wool were then treated with four changes, each of four litres, of hydrochloric acid solution at p_H 4, until the p_H of the solution in equilibrium with the tip wool was 5.17 and that in equilibrium with the root wool was 5.15. These p_H values were regarded as being sufficiently close to p_H 4.8 for further treatment to be unnecessary, and the wools were centrifuged and dried in a room maintained at 65 per cent. relative humidity and 72° F. The ash contents of the tip and root wools, determined by igniting known dry weights, treating the residue with nitric and sulphuric acids, and re-igniting, were 0.43 and 0.15 per cent. respectively. An indication that the tip wool had suffered severe damage by exposure to sunlight is afforded by the fact that a fibre set in boiling 2 per cent. borax

the side and shoulder of the fleece are adversely affected by light over a considerable length at the tip, the root ends appear to be intact, as shown by the determinations of sulphur content given in Table I. From each of a number of staples taken from the side and shoulder of a hogget fleece of 48's - 50's quality, two-inch lengths were cut off at the tip and at the root, the middle section being rejected. The tip and root wools were then purified by extraction with alcohol and ether in a Soxhlet apparatus, followed by repeated washing in distilled water. In this way,

¹² Speakman and Stott, *Trans. Faraday Soc.*, 1934, **30**, 539.

solution¹³ for 30 minutes at 35.4 per cent. extension retained only 10.9 per cent. set after 60 minutes' release in boiling water, whereas the set retained by root wool under similar conditions was 20.3 per cent. In addition, the tip wool, unlike intact fibres, contracted to a length less than the original length in boiling borax and sodium sulphite solutions.

Approximately 2.5 g. samples of air-dry tip and root wool were dried to constant weight *in vacuo* over phosphorus pentoxide, and each sample was then immersed in 200 c.c. of HCl or 150 c.c. of NaOH solution of known p_H at 22.2° C. for two days. Precautions were taken to exclude carbon dioxide from the alkaline solutions during equilibration and p_H measurement. The amounts of acid and alkali combined with the wools were calculated from the measurements of initial and final p_H , except at extremes of p_H where aliquots of the original and equilibrium solutions were titrated with alkali or acid. From the results, which are collected in Table II, the titration curves shown in Fig. 1 were constructed. It should be noted that the acid-titration curve of tip wool has been corrected for the amount of acid combined at p_H 5, which is presumably due to the high ash content already noted.

Discussion of Results.

Since the acid-titration curves of tip and root wool are practically identical, there can be no doubt that the main peptide chains of animal

TABLE II.

Wool.	Reagent.	Final p_H .	C.c. N/1 Acid or Alkali Combined with 100 g. Dry Wool.	
			p_H .	Titration.
Root	HCl	1.18	—	75.8
		1.66	—	67.8
		2.32	—	41.2
		2.93	18.7	—
		3.52	7.6	—
		3.98	2.0	—
Tip	HCl	1.13	—	76.1
		1.66	—	67.2
		2.32	—	42.3
		2.93	18.6	—
		3.67	6.5	—
		5.00	2.9	—
Root	NaOH	12.00	—	145.7
		11.95	—	60.8
		11.82	—	29.0
		11.42	10.8	—
		11.35	13.2	—
		11.30	9.7	—
		11.15	11.2	—
		10.94	11.0	—
		10.80	12.1	—
		10.56	9.5	—
		10.10	7.3	—
		9.52	4.9	—
		9.13	4.9	—
		8.70	3.8	—
		8.18	3.1	—
Tip	NaOH	7.18	2.0	—
		6.80	1.3	—
		12.00	—	155.3
		11.95	—	80.2
		11.68	—	35.9
		11.24	16.8	—
		11.20	18.4	—
		10.80	16.4	—
		10.77	19.7	—
		10.65	15.7	—
		9.84	15.1	—
		8.96	11.8	—
		8.63	8.2	—
		8.09	5.2	—
		7.80	4.9	—
		7.66	3.8	—
		7.60	2.2	—
		7.50	3.1	—
		6.86	1.8	—
		6.80	1.3	—

¹³ Speakman, *J. Soc. Dyers and Colourists*, 1936, **52**, 335.

fibres are not hydrolysed by water vapour under the influence of sunlight.¹⁷ The alkali-titration curves, on the other hand, are by no means identical, the difference in affinity for alkali at p_H 10 being about 8.0 c.c., of $N/1$ NaOH/100 g. dry wool. On examining the tip and root wools by means of Feigl's sodium azide-iodine reagent, the presence of excess sulphhydryl groups in the tip wool was readily revealed, traces only being detected in the root wool. It seems reasonable, therefore, to refer the increased affinity of tip wool for alkali to the sulphhydryl groups which are produced when disulphide bonds are hydrolysed under the influence of sunlight. In support of this conclusion, the dissociation constant of the groups responsible for the extra alkali-combining capacity of tip wool was found to be 3×10^{-9} , by plotting the difference between the alkali-titration curves of tip and root wools, and one of the dissociation constants of cysteine¹⁴ is about 7×10^{-9} . Finally, if the sulphenic acid groups formed at the same time as the sulphhydryl groups decompose completely into aldehyde, which is readily detected in tip wool by means of Schiff's reagent, the increased affinity of tip wool for alkali should be equivalent to the sulphur lost during exposure to sunlight. On this basis, the amount of sulphur lost by the tip wool used in the preceding experiments would be about 0.26 per cent. on the dry weight, which is less than that recorded for similar wool in Table I. The difference, if real, suggests that sulphur may be lost from wool without leaving a corresponding number of sulphhydryl groups in the fibre. A possible mechanism, not involving the intervention of water, has been advanced by Nicolet¹⁵ and this will receive discussion in a later paper. It should here be mentioned, however, that the disulphide bonds of *dry* fibres are readily decomposed under the influence of ultraviolet light. Hence although there can be little doubt that the main change experienced by the disulphide bonds of animal fibres on exposure to air, water vapour and sunlight is similar to the main reaction taking place in caustic soda solution, the possibility of simultaneous reactions of a different character must not be rejected.

Reference must now be made to the previously published titration curve of Cotswold wool.¹² When the latter was prepared for experiment, the extent to which wool fibres undergo decomposition in sunlight was insufficiently appreciated, and no effort was made to separate and use intact root wool. In consequence, the fibres contained sulphhydryl groups arising from disulphide bond breakdown, and the alkali-titration curve showed a step at p_H 10. Combination with alkali was attributed to the back titration of lysine side chains in salt linkages, on the assumption that the dissociation constant of the ϵ -amino group of lysine is 3.2×10^{-5} . Edsall and Blanchard¹⁶ have since shown, however, that the ϵ -amino group takes part in zwitterion formation, and has a much higher dissociation constant than was formerly assumed. There is thus no difficulty in referring the large amount of alkali combined with Cotswold wool at p_H 10 mainly to the presence of a high proportion of sulphhydryl groups, especially as the similar step on the titration curve of New Zealand tip wool is missing from the corresponding curve for root wool. The latter curve, which may be regarded as having general validity for intact wool keratin, has the further importance of showing that wool,

¹⁴ Cannan and Knight, *Biochem. J.*, 1927, **21**, 1384.

¹⁵ Nicolet, *J. Amer. Chem. Soc.*, 1931, **55**, 3066.

¹⁶ Edsall and Blanchard, *ibid.*, 1933, **55**, 2337.

¹⁷ See Rideal and Mitchell, *Proc. Roy. Soc., A*, 1936, **155**, 698; 1937, **159**, 206.

besides possessing an isoelectric range, combines with little alkali below p_H 10, in agreement with the salt linkage hypothesis.

Summary.

The titration curves of root and tip wool, taken from staples selected from the side and shoulder of a New Zealand Romney fleece, have been determined with a view to interpreting the decomposition undergone by wool fibres on exposure to sunlight during growth. Since the acid titration curves of intact (root) and exposed (tip) wools are practically identical, there can be no doubt that the main peptide chains of animal fibres are not hydrolysed under the influence of sunlight and air. The disulphide bonds, on the other hand, are severely attacked, undergoing similar changes to the main reaction taking place in caustic soda solution. Aldehyde and sulphydryl groups are developed, the latter being responsible for the increased affinity of exposed (tip) wool for alkali above p_H 7. The titration curve of root wool may be regarded as having general validity for intact wool keratin, and has the importance of showing that wool, besides possessing an isoelectric range, combines with little alkali below p_H 10, in agreement with the salt linkage hypothesis.

In conclusion, we wish to express our indebtedness to the Government Grant Committee of the Royal Society for a grant in aid of an investigation on the action of light on wool.

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INTERCHANGE REACTIONS OF OXYGEN.

1. INTERCHANGE OF OXYGEN BETWEEN WATER AND POTASSIUM PHOSPHATE IN SOLUTION.

BY E. BLUMENTHAL AND J. B. M. HERBERT.

Received 29th April, 1937.

It was suggested to us that it might be possible to obtain information regarding phosphate metabolism in the body by feeding animals with phosphate containing the O^{18} isotope in excess of the normal. This "shifted oxygen" would then serve as an indicator and enable the course of the phosphate through the body to be followed.

For this method to be feasible it has to be shown that the oxygen of the phosphate remains in the phosphate and does not exchange with the oxygen contained in other constituents of the body, *e.g.*, water.

The present paper deals with the investigation of this latter problem. The results described below show that such exchange does in fact take place and that the original experiment outlined above is therefore not feasible. The exchange, however, was deemed of sufficient interest to merit the investigation which forms the subject of the present paper.

Experimental.

"Heavy Oxygen" Water.—This was prepared by a fractional diffusion method using the mercury vapour diffusion pumps described by Hertz¹ and Barwich.²

¹G. Hertz, *Z. Physik*, 1934, **91**, 810.

²Barwich, *ibid.*, 1936, **100**, 167.

The resulting water had a density about 300 parts per million greater than that of normal water at the same temperature (0°C). It was usually diluted with normal water before use in the experiments described below, in order to economise material.

Potassium Orthophosphate (K_3PO_4).—It was found impossible to obtain this salt in a very high state of purity owing to hydrolysis in solution and subsequent formation of carbonate. The crystalline salt only loses the last traces of water at 300° – 400°C . Any water of crystallisation remaining however merely acts as a diluent of the heavy oxygen water used as solvent and the results are easily corrected for this effect.

The two specimens of phosphate used analysed as follows:

- (A) K_3PO_4 83 per cent.; H_2O 14.5 per cent.; $\text{K}_2\text{CO}_3 + \text{KOH}$ 2.5 per cent.
 (B) K_3PO_4 93 per cent.; H_2O 5.8 per cent.; $\text{K}_2\text{CO}_3 + \text{KOH}$ 1.2 per cent.

The Exchange Reaction.

From 10–30 mgm. of the phosphate were accurately weighed out into a small glass vessel closed with a tap and fitted with a ground joint for attachment to a vacuum line. The vessel was then evacuated by means of a mercury vapour pump and rather more than sufficient "heavy" water to make a saturated solution at room temperature was distilled into it. In the bulk of the experiments this was done by allowing the water to evaporate from a storage vessel into a large evacuated flask of known volume until the water vapour pressure reached the desired value. The storage vessel was then shut off and the water vapour condensed onto the phosphate by a freezing mixture at -80°C .

It was later found that this method tended to give low results, *i.e.*, the weight of water condensed was less than that calculated from the pressure measurement. In the later experiments therefore the amount of water condensed onto the phosphate was determined directly by weighing the reaction vessel before and after the addition of the water.

After a time varying from three to sixty hours the water was distilled off *in vacuo* from the phosphate at 0°C . into a storage vessel containing a little gold foil. It was left in contact with the gold for twenty-four hours in order to remove traces of mercury vapour from the manometers, etc., and was then distilled *in vacuo* from this vessel at -10°C . to a second vessel at -30°C .

Its density was then measured using the micropyknometer described by Gilfillan and Polanyi.³

TABLE I.

Number of Expt.	Duration (Hours).	$\Delta\rho$ (Initial).	$\Delta\rho$ (Final).	$\Delta\rho$ (Equilibrium).
1	12	0	— 4	0
2	13	160	86	118
3	23	160	109	118
4	61	160	101	118
5	7	160	111	118
6	3	160	99	118
7	18	280	214	206
8	18	200	174	160

by Gilfillan and Polanyi.³ It was found impossible to carry out experiments of less than two hours' duration owing to the time taken for the salt to dissolve in the water and that required to distil off sufficient water for a density measurement.

Results.

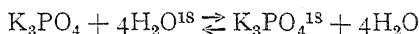
The results obtained are shown in Table I.

" $\Delta\rho$ initial" is the excess density, in parts per million, of the water at the commencement of the experiment and " $\Delta\rho$ final" is that of the water re-

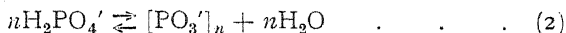
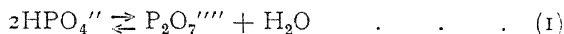
³ Gilfillan and Polanyi, *Z. physik. Chem.*, 1933, 166, 254.

moved from the reaction vessel at the end of the experiment. Both are referred to normal water at the same temperature ($0^{\circ}\text{C}.$). The last column, " $\Delta\rho$ equilibrium" gives the value of the density excess of the water to be expected when equilibrium has been attained calculated on the assumption that the o^{18} isotope is evenly distributed throughout the oxygen of the water and of the phosphate. The results have been corrected for the water content of the solid phosphate taken. The error in the density measurement is estimated to be about ± 10 parts per million.

It appears from these results that equilibrium is established in less than three hours at room temperature (17° to $22^{\circ}\text{C}.$) and that exchange takes place between the oxygen of the water and certainly three, probably all four, of the oxygen atoms in the phosphate thus:



It was originally expected that a slow exchange would take place through one or both of the following reactions:—



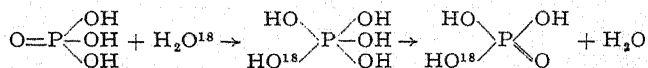
The exchange would take place by the water molecule which is liberated in the forward reaction being substituted by a "heavy oxygen water" molecule in the back reaction.

According to Weber⁴ a solution of sodium pyrophosphate is not detectably transformed into orthophosphate on standing or boiling for some time if the solution is alkaline. If the solution is acid a slow change to ortho-phosphate takes place, some 90 to 95 per cent. of the latter being formed at equilibrium. We failed to detect the formation of pyrophosphate after refluxing a saturated solution of potassium orthophosphate for four days.

The second reaction has been studied by Warschauer⁵ who showed that the soluble metaphosphates are stable except in strongly acid solutions, when change over to orthophosphate takes place.

Hence in our experiments, in which the solution was always alkaline, the observed rate of exchange cannot be accounted for by the above mechanism.

Further, X-ray crystallographic study of the phosphates⁶ has shown that in the crystal at any rate the PO_4 ion consists of four close-packed oxygen atoms arranged in the form of a tetrahedron around a central, totally screened, phosphorus atom. If the screening persists in solution it precludes the possibility of exchange through the formation of an unstable penta-hydroxy compound thus:



The following mechanism is suggested to account for our results.

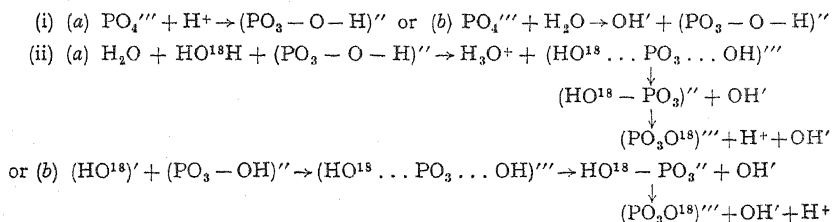
A proton attacks one of the oxygen atoms of the PO_4 ion weakening the O—P bond and allowing it to stretch out thus lessening the screening of the phosphorus atom. A hydroxyl ion from the water pushes into the phosphorus atom as the bond stretches and replaces the original

⁴ J. Weber, *Pogg. Annalen*, 1848, **73**, 148.

⁵ F. Warschauer, *Z. anorg. Chem.*, 1903, **36**, 137.

⁶ J. West, *Z. Kristall.*, 1930, **74**, 306.

hydroxyl, subsequently dropping off its proton and reforming the PO_4 ion with one of the original oxygen atoms exchanged for one from the water thus:



In a solution rich in H^+ the reaction would take place by steps 1a and 2a while in alkaline solution 1b and 2b appear more probable. Actually of course solutions of potassium phosphate (K_3PO_4) contain considerable concentrations of HPO_4'' and OH' owing to hydrolysis.

We hope to extend the investigation to the anions of other oxyacids.

Our best thanks are due to Professor Polanyi and Mr. M. G. Evans for much helpful advice and criticism and to Mr. R. Gilson for his help in connection with the erection of the diffusion pumps and other necessary apparatus.

Summary.

A method is described for the investigation of the exchange of oxygen atoms between water and potassium phosphate in solution using the heavy oxygen isotope as "indicator."

It is shown that rapid interchange takes place between the oxygen atoms of the phosphate and that of the water.

*The University,
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THE ELECTRON DIFFRACTION INVESTIGATION OF SOME INORGANIC HALIDES.

BY A. H. GREGG, G. C. HAMPSON, G. I. JENKINS, P. L. F. JONES, AND
L. E. SUTTON.

Received 30th April, 1937.

In 1934 L. O. Brockway and F. T. Wall¹ showed that the lengths of the bonds in several non-metallic halides are less than the values calculated by the empirical rule of additivity of atomic covalent radii which was enunciated independently and almost simultaneously by L. Pauling² and N. V. Sidgwick.³ The evidence in support of the rule is sufficient for it to be evident that the considerable discrepancies observed in these halides are systematic abnormalities. Brockway and

¹ L. O. Brockway and F. T. Wall, *J. Amer. Chem. Soc.*, 1934, **56**, 2373.

² L. Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293.

³ N. V. Sidgwick, *Ann. Repts. Chem. Soc.*, 1931, **28**, 384; *The Covalent Link in Chemistry*, Cornell, 1933, p. 82.

Wall suggested two possible causes for them: (1) polar character of the bonds, *i.e.*, that the bonds, being not pure covalencies but resonance hybrids between these and pure polar bonds,⁴ *e.g.*, $X-Cl$ and X^+Cl^- , are stronger,⁵ thus have greater stretching force constants, and so by Badger's empirical rule⁶ are shorter than pure covalencies would be: (2) partial double bond character of the bonds, *i.e.*, that the bonds, formerly thought to be single bonds, are actually resonance hybrids between single and double bonds, owing to contribution by such struc-

tures as $Cl \overset{Cl}{\rightleftharpoons} Si-Cl$ and $Cl \overset{Cl}{\rightleftharpoons} Si \overset{Cl}{\leftarrow} Cl$ in the case of silicon tetra-

chloride, with the result that the distance is less than that for a single bond.⁷ They decided, however, that the evidence then available did not suffice for a choice to be made between these hypotheses.

More recently L. O. Brockway and H. O. Jenkins⁸ published results which, they claim, enable this to be done. They argued that whereas it is possible that partial double bond character may exist in the halides, owing to the unshared electrons which a mono-covalent halogen atom possesses, this would not be possible in the corresponding methyl derivatives. Since in actual fact the latter prove to have perfectly normal distances, the second hypothesis was deemed to be correct. This argument obviously is valid only if it can be shown independently either that the substitution of methyl groups for halide atoms does not change the ionic character of the bonds (*i.e.*, the relative importance of the structures

$A:B$, $\bar{A}:\bar{B}$, $\bar{A}:\bar{A}:\bar{B}$) or that the effects of change therein would be too small to account for the observed discrepancies. It is obvious, whatever independent evidence be used to determine the polar character of the bonds, *e.g.*, electric dipole moments^{9,10} or abnormalities of heats of formation,⁵ that the first proviso is not satisfied; Brockway and H. O. Jenkins therefore endeavoured to show that the second one is. They stated that although the differences in electro-negativity of the bonded atoms are greater in some of the methyl derivatives than in the chlorides, no deviations in the former class from additivity of the covalent radii are observed, and therefore that the discrepancies in the chlorides must be due to some other cause. Although they do not say so, it is to be presumed that the comparison is not to be restricted to the methyl and chloro derivatives of the same element, for then the only suitable one for which the necessary data are available is oxygen, and although the C—O bond is normal the Cl—O bond is 0.03 Å.^{11,12} longer than the calculated value. If we may compare say the C—O bond and the P—Cl bond, which have approximately equal differences of electro-negativity on Pauling's scale, then it is true that although the former is normal the latter is 0.09 Å short. Before accepting this argument as conclusive it may be desired that the significance of this electronegativity

⁴ L. Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 988.

⁵ L. Pauling, *ibid.*, 1932, **54**, 3570.

⁶ R. M. Badger, *J. Chem. Physics*, 1934, **2**, 128.

⁷ L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2705.

⁸ L. O. Brockway and H. O. Jenkins, *ibid.*, 1936, **58**, 2036.

⁹ N. V. Sidgwick, *The Covalent Link in Chemistry*, Cornell, 1933, p. 151.

¹⁰ M. G. Malone, *J. Chem. Physics*, 1933, **1**, 197; M. G. Malone and A. L. Ferguson, *ibid.*, 1934, **2**, 99.

¹¹ L. E. Sutton and L. O. Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473.

¹² L. Pauling and L. O. Brockway, *ibid.*, 1935, **57**, 2684.

scale should be more certain than it is at present; thus, it predicts that in the C—I and C—S bonds carbon is the negative atom, whereas electric dipole moment measurements show unambiguously that the converse is true.^{9, 13, 14}

A further difficulty in the way of explaining the results by single-double bond resonance, which Brockway and H. O. Jenkins recognised, is that in some compounds the bonds become even shorter than double bonds, for these are about 10 per cent. shorter than single bonds, but in silicon tetrafluoride and phosphorus trifluoride the shortenings are 15 per cent. and 13 per cent. respectively.*

It therefore seems useful to seek a further test which may enable a choice to be made between the two explanations, and to apply it. Such a test is suggested by considering the factors which would control the relative importance of the double bond structures in the case of a series of compounds having different groups attached to the same central atom. These should be the same as those which control the importance of similar structures when the groups are attached to a benzene ring, *i.e.*, a specific factor for the type of element, and the polarisability factor, and hence for a series involving only related elements the second of these should be the deciding factor (*cf.* Marsden and Sutton).¹⁵ The more polarisable the attached group is, the more readily it should form a double bond by donation of electrons to the central atom or the benzene ring. In the case of the phenyl halides, at least, there is evidence from electric dipole moment data that this is indeed true, for the differences between the moments of aromatic and aliphatic compounds increase from the fluoride to the iodide.^{16, 17} It would therefore be anticipated that the proportional abnormality in distance would also increase from the fluoride to the iodide if it were due to double bond character of the link joining it to the central atom.

On the other hand, the increase of polarisability of the halide, in accordance with the general principles of Fajan's rules, causes the polar character of the bond to decrease from fluoride to iodide, and that this actually occurs is shown by the electric dipole moments of the molecules (see footnote, p. 856). Therefore any abnormality in distance due primarily to this cause should decrease in this order. Thus, by examining complete series of halides, so far as possible, and determining the manner of the variation of the abnormalities it should be possible to distinguish between the two possible causes.

Accordingly, those halides of phosphorus, arsenic, and antimony which had not previously been examined by electron diffraction were investigated, and the halides of mercury and the chloride of boron were re-investigated; mercury dimethyl was also examined in order to obtain a normal covalent radius for mercury.

¹³ E. Bergmann and M. Tschudnowsky, *Z. physikal. Chem., B*, 1932, **17**, 107 *idem.*, 457.

¹⁴ G. C. Hampson, R. H. Farmer, and L. E. Sutton, *Proc. Roy. Soc., A*, 1933, **143**, 147.

* W. G. Penney¹⁴ has concluded that the carbon-carbon double bond distance is really 1.33 Å. and not 1.38 Å., the value used by Pauling, Brockway, and Beach⁷. Pauling has recently informed us, in a private communication, that he and Brockway have now revised their value to 1.34 Å. The double bond is therefore 13 per cent. shorter than the single bond.

¹⁵ R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 599.

¹⁶ L. E. Sutton, *Proc. Roy. Soc., A*, 1931, **133**, 668.

¹⁷ L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1935, 971.

The mercury-carbon distance was found to be 2.23 ± 0.04 Å., which is, within the limits of experimental error, the same as the value reported by Brockway and H. O. Jenkins,⁸ 2.20 ± 0.10 Å. The value is also in good agreement with the calculated one, 2.25 Å., obtained as the sum of the covalent radii given by Pauling and Huggins¹⁸ who based their mercury value on a determination of the Hg—S distance in the crystal. Since carbon cannot form further stable valencies, no shortening from double bond formation would be expected, nor, moreover, would any from polar character, since electric dipole moment evidence which will be published shortly shows that the mercury-carbon moment must be zero.

The results for the halides are striking: they are collected together in Table I., where the observed bond length,* the calculated one,† the difference, and the percentage difference relative to the theoretical value are given.

They show that the abnormalities increase slightly from chloride to iodide for mercury and boron, but decrease from fluoride to iodide in the fifth group elements, carbon, and silicon, and from fluoride to chloride in boron. From what has been said previously, this indicates that the shortening is not due to the same cause in all cases, but that while in the former elements it is due mainly to the tendency to double bond formation, in the latter it is due mainly to polar character. It must be remembered that it may be possible for both to have effect simultaneously, but to be of different importance: this may be the reason for the mixed behaviour of the boron compounds. It is notable that the former elements do not have an octet of electrons in the outermost group, and that therefore double bond formation can occur without extension of the valency group beyond an octet, whereas in such structures as Cl—Sb—Cl the octet of the latter elements would have to ex-



pand to a decet or a duodecet with two unshared electrons. Thus the division into two classes can be correlated with the well-known tendency to complete the octet when it is incomplete, and the comparative reluctance of certain elements to undergo certain types of octet expansion. While in elements of the second short period and the long periods expansion to a duodecet of shared electrons is very common, owing to the relatively low energy *d* orbitals which can be filled, it is an experimental fact, as pointed out by Sidgwick,²⁰ that in the particular case of the fifth main and B sub-group elements expansion to a group of ten or more, *two of which are unshared*, is found to occur only in those elements, which otherwise exhibit the inert pair phenomenon: for example,

¹⁸ L. Pauling and M. L. Huggins, *Z. Krist.*, 1934, 87, 205.

* These results provide further tests of Badger's rule⁶ for calculating bond lengths from force constants. The values so calculated by Howard and Wilson³⁵ for P—Br and Sb—Cl in phosphorus tribromide and antimony trichloride are 2.31 and 2.30 Å. respectively, i.e., 0.10 high and 0.07 Å. relative to the results now reported.

† The Pauling and Huggins covalent radii for phosphorus and arsenic have been confirmed by Maxwell, Hendricks, and Mosley¹⁹ who determined the phosphorus-phosphorus and arsenic-arsenic distances in P₄ and As₄ and found them to be 2.21 ± 0.02 and 2.44 ± 0.03 Å. respectively, the calculated values being 2.20 and 2.42 Å.

¹⁹ L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Physics*, 1935, 3, 699.

²⁰ N. V. Sidgwick, *Ann. Repts. Chem. Soc.*, 1933, 30, 124.

TABLE I.—BOND LENGTHS AND DEVIATIONS.

Halogen. Central Atom.		F.	Cl.	Br.	I.
Boron	obsd.	1.31§	1.75* ± 0.02	1.87* ± 0.02	
	calcd.	1.53	1.88	2.03	
	diff.	-0.22	-0.12	-0.16	
	%	-14.4	-6.4	-7.9	
Carbon	obsd.	1.36 $\dagger \pm 0.02$	1.755* ± 0.005	1.93* ± 0.03	
	calcd.	1.41	1.76	1.91	
	diff.	-0.05	0.00	+0.02	
	%	-3.5	0	+1.0	
Silicon	obsd.	1.54 $\dagger \pm 0.02$	2.00 $\dagger \pm 0.02$		
	calcd.	1.81	2.16		
	diff.	-0.27	-0.16		
	%	-14.99	-7.4		
Phosphorus	obsd.	1.52 $\dagger \pm 0.04$	2.00 $\dagger \pm 0.02$	2.23 $\dagger \pm 0.01$	2.52 $\dagger 0.01$
	calcd.	1.74	2.09	2.24	2.43
	diff.	-0.22	-0.09	-0.01	+0.09
	%	-12.6	-4.3	0	+3.7
Arsenic	obsd.	1.72 $\dagger \pm 0.02$	2.16 $\dagger \pm 0.03$	2.36 $\dagger \pm 0.02$	2.58 $\dagger \pm 0.01$
	calcd.	1.85	2.20	2.35	2.54
	diff.	-0.13	-0.04	+0.01	+0.04
	%	-7.0	-1.8	0	+1.6
Antimony	obsd.		2.37 $\dagger \pm 0.02$	2.52 $\dagger \pm 0.02$	2.75 $\dagger \pm 0.02$
	calcd.		2.40	2.55	2.74
	diff.		-0.03	-0.03	+0.01
	%		-1.25	-1.2	0
Mercury	obsd.		2.34 $\dagger \pm 0.01$	2.44 $\dagger \pm 0.01$	2.61 $\dagger \pm 0.01$
	calcd.		2.45	2.60	2.79
	diff.		-0.11	-0.16	-0.18
	%		-4.5	-6.1	-6.5

* Brockway.²¹ \dagger Brockway and Wall.¹ \dagger Present research. \S Braune and Pinnow.³⁶

compounds of the type $K[SbCl_4]$ and $K[SbBr_4]$ are quite stable, the corresponding arsenic compounds, although known, are very unstable, while phosphorus gives no complex anions of this type at all. From this analogy it would be expected that only in antimony would double bond character be pronounced; actually it appears to be unimportant even then.

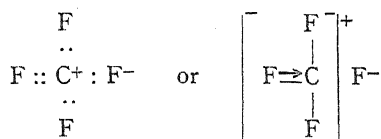
Up to this point, the two simple hypotheses advanced by Brockway and Wall appear to explain the facts. There is, however, a considerable difficulty in the way of explaining the abnormalities in the fifth group by polar character, for while they change as anticipated on this hypothesis if we consider the same central atom with different halogens, they fail to do this if we consider the same halogen attached to different central atoms. Thus, the polarity of the P—Cl, As—Cl, and Sb—Cl bonds increases in this order,^{||} but the observed abnormalities

²¹ L. O. Brockway, *Rev. Mod. Physics*, 1936, 8, 260.

\parallel The qualitative order required for such discussion is given sufficiently clearly by the electric dipole moments of the molecules themselves; for the series AsF_3 , $AsCl_3$, $AsBr_3$, and AsI_3 these are 2.65, 2.17, 1.63, and 0.96 respectively; and for the series PCl_3 , $AsCl_3$, and $SbCl_3$ they are 1.16, 2.17, and 3.12 respectively.

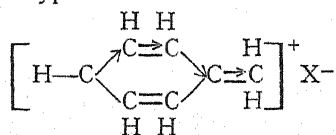
decrease. This observed order is, indeed, what would be predicted on the double bond hypothesis, for the power of the central atom to deform the halogen decreases as the atomic weight increases. It therefore appears that the two hypotheses as they stand are not sufficient to explain all the anomalies so far observed.

One of the reasons why Brockway and Wall suggested that ionic character might cause bond shortening is that the carbon-fluorine distance in carbon tetrafluoride is 0.05 Å. shorter than the calculated value. Brockway and H. O. Jenkins report, however, that there is no such shortening in the bond in methyl fluoride, and because of this and their abandonment of the polar character hypothesis Pauling has suggested that the C—F bonds in the former compound may have double bond character, because the very polar character of the bond makes possible an important contribution to the character of the molecule by four similar structures, each "having an F⁻ ion and a CF₃⁺ ion in which one double bond and two single covalent bonds are formed."



It is not entirely certain that there is any discrepancy between the fluorides which calls for an explanation, inasmuch as the experimental error in the tetrafluoride is given as ± 0.02 Å., as is also that in methyl fluoride, and the difference in question is only 0.05 Å.* It is therefore profitable to see whether or not there is independent evidence of resonance of this general type, and whether it happens with halogens other than fluorine.

We may compare the increases in *meta*-directing power caused by replacing hydrogen in the methyl group of toluene by fluorine or chlorine. Thus, whereas toluene gives only 4 per cent. of the *meta* derivative on nitration, benzyl chloride gives 12–15.5 per cent., and benzyl fluoride 17.5 per cent.;²² benzotrichloride gives 64.5–74.8 per cent.,^{23, 24} and benzotrifluoride 99 per cent.²⁵ These facts may be considered to show that structures of the type



are relatively more important when X is fluorine than when it is chlorine, but the two halogens are not greatly different in their influence. Another instance, involving however an equilibrium and not rates of irreversible reactions, is the change of acid strength produced in acetic acid by the substitution of fluorine and chlorine for hydrogen. The dissociation

* Note added 9/6/37. Dr. G. B. B. M. Sutherland informs us that recalculation of infra red data for methyl fluoride (resolution of line spacing) reported by Bennett and Meyer (*Physic. Rev.*, 1928, **32**, 888) gives $l_{\text{C-F}} = 1.37 \pm 0.005$ Å.; this is equal to Brockway and Walls' value for $l_{\text{C-F}}$ in carbon tetrafluoride.

²² C. K. Ingold, and E. H. Ingold, *J. Chem. Soc.*, 1928, 2249.

²³ A. F. Hollemann, *Chem. Rev.*, 1924, **1**, 187.

²⁴ Spreckels, *Ber. Deutsch. Chem. Ges.*, 1919, **52**, 315.

²⁵ F. Swarts, *Bull. Acad. roy. Belgique*, 1920, 399; *Chem. Zentr.*, 1921, iii, 32.

constant of acetic acid is 1.856×10^{-5} at 25° , that of dichloroacetic acid is 0.0514 at 25° , and that of difluoroacetic acid is $0.0571 - 0.0574$.²⁶ Here again fluorine has the greater effect, but the ratio is not large. The polar characters of the C—F and C—Cl bonds, calculated as the quotient of the electric dipole moment and the bond length, are 0.2675 and 0.2202 respectively, and it is possibly significant that the ratio of these values, 1.215, is nearly equal to that of the dissociation constants quoted above.

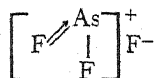
Further evidence that in benzotrichloride such structures participate is that the electric dipole moment of this compound is -2.07 whereas that of methyl chloroform is -1.57 , the difference -0.5 being attributed to the hybridisation.¹⁶ Corresponding measurements for the fluorine compounds are not available.

Facts which are less easy to interpret in this connection are that whereas triphenyl methyl chloride, bromide, and iodine react readily with metals, the fluoride does not; it is reported²⁷ to be entirely unaffected by silver, mercury, zinc, copper, bronze or magnesium, even when boiled with excess silver for six hours. Moreover, the chloride, bromide and iodide give conducting solutions in liquid sulphur dioxide, and the order of dissociation²⁸ is $\text{Cl} < \text{Br} \geq \text{I}$. If the ease of breakage

of the link to give two ions is a measure of the ionic character of the unbroken bond, these facts would reverse the order of electronegativity of the halogens. It is probable that this simple correlation is unsound; rather it would seem that ionisation occurs after a non-ionic fission.

Considering all these facts, it is clear that there is considerable evidence for resonance with structures of the general type which Pauling suggested, and for the importance of these structures being greater, but not vastly so, in the fluorine compounds than in the chlorine ones.

Such resonance may be regarded as a secondary consequence of the primary resonance of a key bond between covalent and polar structures, and it may be of frequent occurrence. It can be used to explain other bond shortenings which have been attributed to polar character of bonds, such as those in the fifth group trihalides previously discussed, for it is possible to write such structures as:—



for these compounds. The fall in the deforming power of the central atom with increase of atomic number might then be held to account for the fall in the percentage shortening, which was previously remarked upon as a stumbling block in the way of the theory of direct polar effect (p. 857).

Until further data are available, no final decision as to the correctness or otherwise of this explanation can be made.

It is an interesting fact that double-bonded structures cannot be drawn without increasing the octet when the central atom becomes negative in the polar structure. Thus, although in trimethyl amine,

²⁶ F. Swarts, *Chem. Zentr.*, 1903, ii, 710.

²⁷ F. F. Blicke, *J. Amer. Chem. Soc.*, 1924, 46, 1515.

²⁸ P. Walden, *Ber. Deutsch. Chem. Ges.*, 1902, 35, 2024; *Z. physikal. Chem.*, 1903, 43, 455.

dimethyl ether, and methyl chloride it is possible to formulate structures which permit a methyl carbon atom to form a double bond to the central atom, by primary ionisation of a hydrogen-carbon bond, *viz.*, $\text{H}^+\text{CH}_2 = \text{X}^-$, apart from the rather improbable nature of these the above reason absolutely excludes the possibility of shortening from this cause.

Stereochemical Points.—As is explained in detail in the experimental section, it was not possible to decide whether or not the boron tri-chloride molecule is planar. Since the boron-chlorine distance obtained depends upon the valency angle assumed, it is essential to use independent evidence to determine this: the electric dipole moment of this compound is zero^{29, 30} and the angle is therefore 120° .*

It is similarly impossible to determine the configuration of mercury dimethyl, or even of the chloride and the bromide, owing to the relatively small scattering powers of the atoms attached to the mercury atom. In the case of the iodide, however, where the conditions are more favourable, it is possible to show that the angle is at least 160° . This is in agreement with the results of Raman spectra investigations,^{31, 32} and electric dipole moment determinations in the vapour phase,³³ all of which show the molecules to be linear.

The valency angles in all the fifth group trihalides so far examined are remarkably constant, being approximately 100° (Table II.). It is interest-

TABLE II.

Central Atom. \ Halogen X.		F.	Cl.	Br.	I.
Phosphorus . . .	$\text{X}-\widehat{\text{P}}-\text{X}$ $\angle \text{x-x}$	$99 \pm 4^\circ$ 2.37	$100 \pm 2^\circ$ 3.095	$100 \pm 2^\circ$ 3.41	$98 \pm 4^\circ$ 3.80
Arsenic . . .	$\text{X}-\widehat{\text{As}}-\text{X}$ $\angle \text{x-x}$		$101 \pm 4^\circ$ 3.365	$100 \pm 2^\circ$ 3.63	$100 \pm 2^\circ$ 3.95
Antimony . . .	$\text{X}-\widehat{\text{Sb}}-\text{X}$ $\angle \text{x-x}$		$104 \pm 5^\circ$ 3.74	$96 \pm 2^\circ$ 3.81	$98 \pm 2^\circ$ 4.15
Obsd.	$\angle \text{x-x}$		3.7	3.8	4.2
Calcd.	$\angle \text{x-x}$	2.8			

ing to consider these observations in the light of the simple theory of directed valency presented by Pauling.³⁷ According to this, the three valencies formed by a fifth group element in its trivalent state would involve only the utilisation of *p* orbitals of the central atom, and would therefore be mutually perpendicular, unless the combined bond formation energies

²⁹ E. Bergmann and L. Engel, *Physikal. Z.*, 1931, **32**, 507.

* Braune and Pinnow³⁶ have shown, from an electron diffraction investigation that boron trifluoride is planar.

³⁰ W. Nespital, *Z. physikal. Chem.*, B, 1932, **16**, 153.

³¹ P. Krishnamurti, *Ind. J. Physics*, 1930, **5**, 113.

³² H. Braune and G. Engelbrecht, *Z. physikal. Chem.*, B, 1930, **10**, 1; *ibid.*, 1931, **11**, 409.

³³ H. Braune and R. Linke, *ibid.*, 1935, **31**, 12.

³⁴ W. G. Penney, *Proc. Roy. Soc.*, A, 1937, **158**, 306.

³⁵ J. B. Howard, and E. B. Wilson, *J. Chem. Physics*, 1934, **2**, 630.

³⁶ H. Braune and P. Pinnow, *Z. physikal. Chem.*, B, 1937, **35**, 239.

³⁷ L. Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367.

were enough to perturb considerably the independent s and p quantisation, and so to cause s - p hybridisation, in which case the angle might increase up to the tetrahedral value, $109^\circ 28'$. For this to happen, the heat of formation of the molecule from the atoms should be of the order of 400 Kcals. per gm. mol. Now whereas the heats of formation of the hydrides decrease in the order phosphorus, arsenic, antimony, leading to the prediction that the angle would decrease in this order, the heats of formation of the chlorides are approximately equal, being 187, 181, and 204 Kcals./gm. mol., and approximately the same degree of hybridisation and the same angle might therefore be expected in this series. In the series of trihalides of arsenic there is, however, a very marked fall in the heats of formation from the fluoride to the iodide, the values being 317, 181, 144, and 99, for the fluoride, chloride, bromide, and iodide respectively; a notable decrease of angle might therefore be expected, but it is not observed. There are, however, other factors which might affect the angle, and the effect of these must be considered.

Between the attached atoms there are simple electrostatic forces depending upon the polar character of the bonds formed with the central atom, London dispersion forces depending upon the electric polarisability, and what are often called steric repulsions depending upon the effective size of the attached atoms considered as compressible balls. The dispersion and steric forces will tend to fix the distance between the attached atoms at a value depending upon these alone and not upon the central atom, and corresponding to the minimum in potential energy caused by their opposition. In the present case these equilibrium distances should be those observed between non-bonded halogen atoms in crystals, which are 3.7, 3.8, and 4.2 Å. for chlorine, bromine, and iodine respectively. These values correspond to an "envelope" about 0.75 Å. about each atom,³⁸ and if this be used to calculate the non-bonded distance for fluorine a value 2.78 Å. is obtained. It will be noticed that the halogen-halogen distances found in the phosphorus and arsenic tri-halides are less than the above values, the discrepancies being approximately equal in phosphorus and in arsenic compounds, but being greater for the former class than for the latter. There is therefore a decrease in the nett force of repulsion going down a vertical series, and since this is not accompanied by a change of angle, it would be expected that there is some force tending to widen the angle, which increases in this direction. The electrostatic forces do indeed increase down the series, and this may be the compensating effect. In a horizontal row, however, they decrease from left to right, from fluoride to iodide, and there is therefore no obvious effect which can compensate for the decrease in heat of formation mentioned earlier. It is just possible that the process by which the bonds are shortened, whatever it is, may tend to decrease the angle, and thus help oppose any widening from steric effects, going vertically upwards, and compensate for the widening from left to right. It can only be said that if this is so, the perfection of these complicated compensations is remarkable.

The simplest conclusion is that the valency angles are fixed, and functions of the central atoms alone, the forces between the attached atoms being immaterial. This conclusion, however, would seem to require a new theory of directed valency.

³⁸ N. V. Sidgwick, *Ann. Reps. Chem. Soc.*, 1932, **29**, 67.

Experimental.

Apparatus.—The electron diffraction camera and associated equipment used were those described by de Laszlo⁴⁰ with minor modifications. The resistance used in measuring the high voltage was run at the working voltage for 15-20 minutes before readings were taken, by which time it was found to reach temperature equilibrium and to be reliable to within ± 1 per cent. by standardisation with gold-foil photographs. Its present form approximates to that of the one described by Bowdler.³⁹

Measurement and Interpretation of Photographs.—The photographs were taken at various cathode voltages. In order to measure the ring diameters the plates were placed over an aperture in a light tight box and illuminated by a 100 watt "Pearl" lamp placed centrally beneath; the intensity of the light could be controlled by means of a resistance. Experience showed that such illumination is superior to uniform illumination, since it gives good compensation for the rapidly falling background on the plate, and by varying the light intensity any given ring could be made fairly prominent. The diameters were actually measured by setting a fine pointer, attached to the sliding sleeve of a cathetometer, to the places of maximum or minimum apparent intensity. Each visible ring was measured two or three times

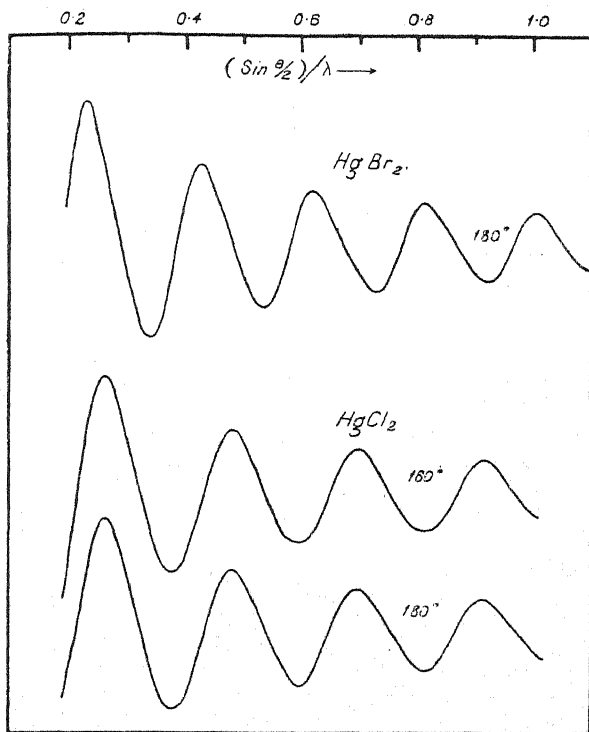


FIG. 1.—Scattering curves for mercuric chloride and mercuric bromide.

and the average value taken. Except in the case of mercury dimethyl visual minima were not used in the interpretation of the photographs, as the eye is less sensitive to them than to the maxima. Many photographs were taken for each substance and only the clearest ones used.

The method of interpretation used was the simple one developed by Wierl⁴¹ and by Pauling⁴² and Brockway.²⁰

Preparation and Purification of Substances.—With the exceptions of mercuric chloride and bromide, arsenic tri-iodide, mercury dimethyl, and

³⁹ G. W. Bowdler, *J. Inst. Elec. Eng.*, 1933, **73**, 65.

⁴⁰ H. de Laszlo, *Proc. Roy. Soc., A*, 1934, **140**, 662.

⁴¹ Wierl, *Ann. Physik*, 1931, **8**, 5, 521.

⁴² L. Pauling and L. O. Brockway, *J. Chem. Physics*, 1934, **2**, 867.

boron trichloride good commercial specimens were used without special purification.

Mercuric Chloride and Bromide were recrystallised from ethyl alcohol and water mixture.

Arsenic Tri-iodide was recrystallised from chloroform.

Mercury Dimethyl was prepared as described by Marvel and Gould⁴³ from mercuric chloride and methyl magnesium iodide. The ether layer was separated, dried with calcium chloride, and carefully fractionated. The fraction boiling 90-92°/750 mm. was used (Marvel and Gould,⁴³ 92°/740 mm.).

Boron Trichloride was fractionally distilled in a stream of dry nitrogen and the middle fraction taken. Any remaining hydrogen chloride was removed by cooling in a freezing mixture and pumping off.

Mercuric Chloride.—The large difference in atomic number of the two constituent atoms makes the production of good plates difficult and

TABLE III.

Max.	No. of Plates.	(sin $\theta/2$)/ λ .		$l_{\text{Hg-X}}$.
		Exptl.	Theor.	
Mercuric Chloride.				
1	12	0.258	0.262	2.356*
2	12	0.474	0.478	2.340
3	12	0.691	0.695	2.333
4	10	0.907	0.910	2.328

Mean value: $l_{\text{Hg-Cl}} = 2.335$.

Average deviation = 0.005.

Final result: $l_{\text{Hg-Cl}} = 2.34 \pm 0.01 \text{ \AA}$.

Mercuric Bromide.

1	12	0.239	0.230	2.502*
2	12	0.450	0.425	2.456
3	12	0.658	0.617	2.438
4	11	0.865	0.811	2.438
5	6	1.070	1.003	2.437

Mean value: $l_{\text{Hg-Br}} = 2.44 \text{ \AA}$.

Average deviation = 0.008 Å.

Final result: $l_{\text{Hg-Br}} = 2.44 \pm 0.01 \text{ \AA}$.

determined (sin $\theta/2$)/ λ value with that obtained from the theoretical curve for the arbitrary assumed value of the mercury-chlorine distance and making the correction by simple proportion. The mean value was derived by rejecting the value from the first maximum (asterisked), which owing to its high intensity gives an unreliable value, and taking the arithmetic mean of the remaining three values.

Mercuric Bromide.—The same remarks apply to this compound as do to the chloride. A determination of the valency angle is impossible from consideration of the diffraction pattern, and the angle was therefore assumed to be 180°. The value of $l_{\text{Hg-Br}}$ assumed was 2.60 Å.

All the plates for this substance contained four evenly spaced maxima which decreased regularly in apparent intensity from the centre outwards. On six plates there was a weak, but well-defined, fifth maximum. The first three showed slight degradation towards the edge of the plate, but

only four visual maxima could be obtained. These were symmetrical and fairly widely spaced at the cathode voltage used and rapidly decreased in intensity towards the outside of the plate.

Theoretical intensity curves for 180° and 160° are given in Fig. 1, the mercury-chlorine distance being taken as 2.32 Å. in each case. They are practically identical, for since the contribution of the chlorine-chlorine term to the total intensity is very small the maxima do not vary very much as the valency angle is changed. A linear model based on the evidence mentioned on p 859 was therefore assumed. The actual interatomic distance in the molecule can be calculated from each visual maxima by comparing the experimentally

⁴³ Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153.

this was much less marked in the two outer ones. As in the case of the chloride, the value calculated from the first maximum is not included in the arithmetic mean.

Mercuric Iodide.—The majority of these plates showed five strong maxima. The atomic background is not so prominent as in the chloride and the bromide, owing to the more favourable atomic number ratio. The maxima appeared asymmetrical, the first three showing pronounced degradation of intensity towards the outside, and the others a less marked effect. The first two rings were consequently very difficult to measure.

Four theoretical intensity curves for valency angles of 180° , 160° , 120° , and 90° respectively are shown in Fig. 2, the mercury-iodine distance used as a basis for calculation being 2.60 \AA . in each case.

Only in the 180° curve is the asymmetry of each maximum very marked; that of the maxima in the 160° curve should hardly be noticeable on the photographs. Such considerations may be regarded as fairly good evidence that the molecule is linear. The mercury-iodine distances calculated from the various curves are given in Table IV. For the same reasons as before, the results obtained from the first intense maximum were omitted when calculating the mean value. The figures for the average deviations also show

that the valency angle in the region of 160° to 180° , since for such simple curves the average deviation should be least when the theoretical curve gives the best correlation with the diffraction pattern. The sine function changes very slowly from 180° to 160° and this fact, together with the predomination of the mercury-iodine term, explains why a more accurate determination of the valency angle is impossible.

Mercury Dimethyl.—In this compound the ratio of coherent atomic to coherent interatomic scattering is exceedingly unfavourable for the production of good photographs, the atomic background all but completely masking the comparatively small fluctuations due to interatomic terms. With carefully chosen time of exposure and temperature (therefore vapour pressure) it was possible to obtain six plates having three visual maxima

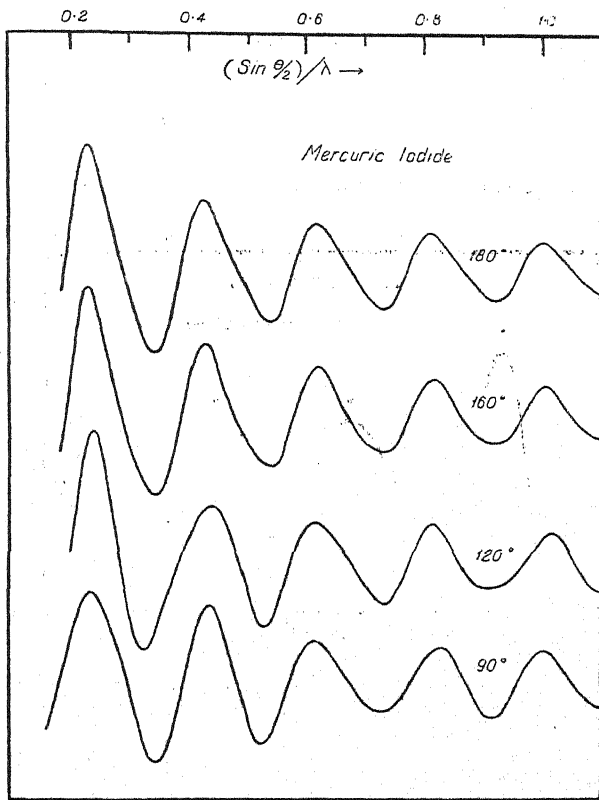


FIG. 2.—Scattering curves for mercuric iodide.

TABLE IV.—MERCURIC IODIDE.

Max. No.	No. of Plates.	$\frac{\sin \theta/2}{\lambda}$ Expt.	$(\sin \theta/2)/\lambda$				$l_{\text{Hg-I}}$			
			180°.	160°.	120°.	90°.	180°.	160°.	120°.	90°.
1	II	0.222	0.228	0.230	0.241	0.236	2.671*	2.694*	2.823*	2.764
2	II	0.417	0.422	0.424	0.442	0.434	2.631	2.644	2.756	2.706
3	II	0.615	0.616	0.618	0.612	0.612	2.604	2.613	2.587	2.587
4	II	0.810	0.808	0.812	0.812	0.826	2.594	2.606	2.606	2.651
5	7	1.001	1.002	1.005	1.016	1.002	2.603	2.610	2.639	2.603
Mean values: $l_{\text{Hg-I}} =$							2.608	2.618	2.647	2.637
Average deviations							0.012	0.013	0.055	0.042

Final value: $l_{\text{Hg-I}} = 2.61 \pm 0.01 \text{ \AA.}$
 $l_{\text{Hg-I}} = 180^\circ$ approx.

and a measurable minimum. The first maximum was very intense and

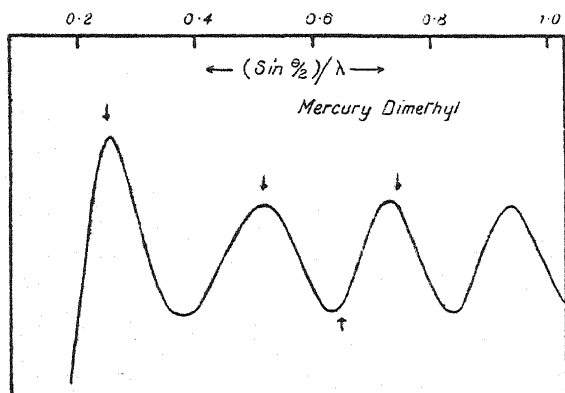


FIG. 3.—Scattering curves for mercury dimethyl.

broad, the second one was fairly strong and symmetrical; the second minimum was quite sharp and was followed by a weak third maximum. In calculating the theoretical intensity curve shown in Fig. 3 the carbon-hydrogen distance was assumed to be 1.14 Å. and the three hydrogen atoms assumed to be tetrahedrally arranged about the carbon atom. The theoretical intensity equation shows that small changes in the carbon angle and in the carbon-hydrogen distances hardly affect the positions of the maxima, and that therefore a determination of the mercury valency angle is impossible. Consequently this angle was taken as 180° . Furthermore, the contribution of the carbon-hydrogen terms to the total intensity is so small that, the mercury angle having been assumed, the carbon-mercury distance can be determined by simple proportion from the experimental and theoretical $(\sin \theta/2)/\lambda$

TABLE V.—MERCURY DIMETHYL.

Max.	Min.	No. of Plates.	$(\sin \theta/2)/\lambda$		$l_{\text{Hg-C}}$
			Exptl.	Calcd.	
1	—	6	0.247	0.253	2.29
2	—	6	0.516	0.517	2.24
—	3	6	0.649	0.630	2.17
3	—	6	0.745	0.732	2.20

Mean value: $l_{\text{Hg-C}} = 2.23 \text{ \AA.}$

Average deviation = 0.04

Final result: $l_{\text{Hg-C}} = 2.23 \pm 0.04 \text{ \AA.}$

values for the maxima and minimum. For calculating the curve $l_{\text{Hg}-\text{C}}$ was taken as 2.24 Å.

Boron Trichloride.—Four photographs of this substance showed six maxima, and three others showed only five. The first two maxima were

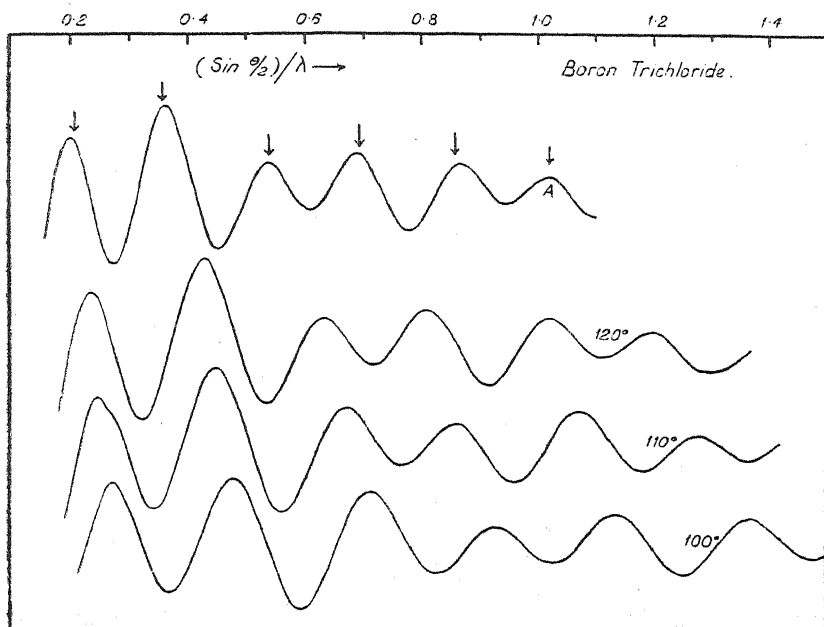


FIG. 4.—Scattering curves for boron trichloride.

very strong and were followed by three medium ones and sometimes one very weak but sharp one. All except the first were symmetrical, regularly spaced, and fairly close under the experimental conditions used.

TABLE VI.—BORON TRICHLORIDE.

Max.	No. of Plates.	$\frac{\sin \theta/2}{\lambda}$ Exptl.	$(\sin \theta/2)/\lambda$ (Calculated).			$l_{\text{B}-\text{Cl}}$		
			120°.	110°.	100°.	120°.	110°.	100°.
1	6	0.210	0.236	0.253	0.274	1.686 *	1.807 *	1.957 *
2	7	0.360	0.428	0.449	0.478	1.783	1.871	1.992
3	7	0.540	0.632	0.669	0.712	1.756	1.858	1.978
4	7	0.698	0.808	0.855	0.926	1.736	1.837	1.990
5	6	0.857	1.016	1.070	1.132	1.778	1.873	1.981
6	4	1.020	1.194	1.276	1.366	1.756	1.876	2.009
Weighted mean: $l_{\text{B}-\text{Cl}} =$						1.762	1.863	1.990
Average deviation . . .						0.015	0.012	0.009

Final value: $l_{\text{B}-\text{Cl}} = 1.76 \pm 0.02$ Å.

The theoretical intensity curves shown in Fig. 4 are for various valency angles and a boron-chlorine distance of 1.50 Å. As they show, the inter-halogen terms are predominant and so, for a fixed chlorine-chlorine distance, small variations in the boron-chlorine distance, or of the boron

valency angle, hardly affect the relative positions of the maxima: the absolute positions of the maxima differ appreciably from curve to curve but the ratios of the $(\sin \theta/2)/\lambda$ values vary very little. There are some small differences in relative intensity; thus in the 120° curve the fourth maxima is stronger than the third, whereas in the 110° and 100° curves the fourth is the weaker. Visually it appeared that the third maximum was stronger than the fourth, but if the valency angle is 110° or 100° as this would indicate the fifth maximum should be stronger than the fourth, which appeared not to be the case. The differences in relative intensities are so small in this compound that a fixation of the angle by such qualitative considerations is unsatisfactory.

The average deviation is least for the 100° curve but they are so small

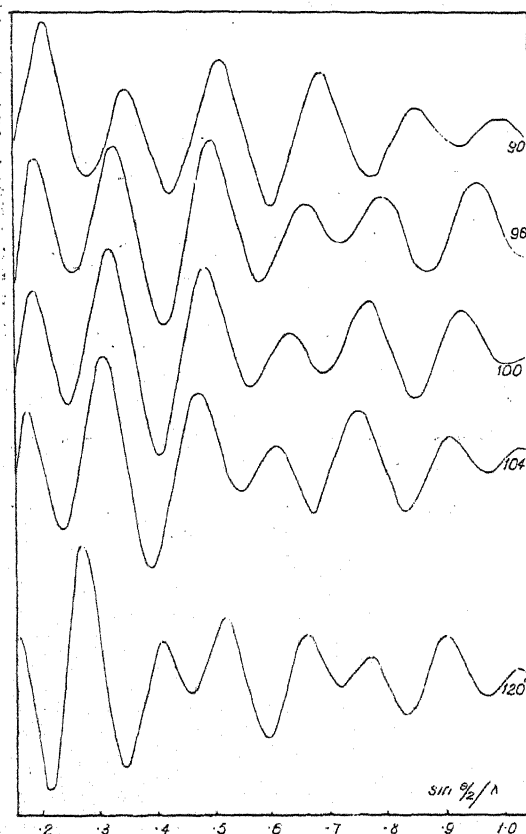


FIG. 5.—Scattering curves for phosphorus tribromide.

fifth and sixth maxima of approximately equal intensity as found experimentally. The quantitative data for all the models are given in Table VII., the value of l_{P-Br} taken in calculating the curves being 2.40 \AA . It will be seen that the 100° model is the one which gives the most constant values for the interatomic distance, this is therefore taken to be the correct structure for phosphorus tribromide, the corresponding phosphorus bromine distance being $2.23 \pm 0.01 \text{ \AA}$.

Phosphorus Tri-iodide.—The phosphorus tri-iodide plates showed a series of six very symmetrical and well-defined rings. As with the tri-

for all the curves that this probably is not a good criterion in this case. In view of the zero dipole moment of boron trichloride (p. 859), a planar model is assumed, whence the value 1.76 \AA is derived for l_{B-Cl} . This distance is used in the calculation of the upper curve in Fig. 4 in order to show the agreement between the observed and calculated values.

Phosphorus Tribromide.—The photographs for phosphorus tribromide showed three very intense inner rings followed by a weak ring and two stronger rings of approximately the same intensity, while on four of the plates a further very weak, but well-defined maximum was just visible. All the rings were symmetrical. The large difference in intensity between the first three rings and the remainder seems to indicate an angle of about 100° . The 100° model also gives a weak fourth maximum and

TABLE VII.—PHOSPHORUS TRIBROMIDE.

Max.	No. of Measurements.	$\frac{\sin \theta/2}{\lambda}$ Exptl.	$(\sin \theta/2)/\lambda$						$l_{\text{P-Br}}$					
			90°.	96°.	100°.	106°.	110°.	120°.	90°.	96°.	100°.	106°.	110°.	120°.
2	12	0.322	0.320	0.304	0.295	0.283	0.280	0.266	(2.38)	(2.26)	(2.20)	(2.11)	(2.09)	(1.98)
3	11	0.477	0.475	0.456	0.444	0.430	0.421	0.397	2.39	2.29	2.23	2.16	2.12	2.00
4	11	0.617	0.636	0.602	0.577	0.546	0.532	0.501	2.47	2.34	2.24	2.12	2.07	1.95
5	12	0.759	0.771	0.721	0.704	0.681	0.669	0.637	2.45	2.28	2.22	2.15	2.11	2.01
6	11	0.913	0.913	0.880	0.854	0.822	0.800	0.741	2.39	2.31	2.24	2.15	2.10	1.94
7	4	1.058	1.090	1.023	0.978	0.933	0.914	0.871	2.47	2.32	2.22	2.12	2.07	1.98
Average . . .									2.42	2.31	2.23	2.14	2.09	1.97
Average deviations									0.04	0.02	0.01	0.02	0.02	0.03

Final results: $l_{\text{P-Br}} = 2.23 \pm 0.01 \text{ \AA.}$; $\text{Br}-\hat{\text{P}}-\text{Br} = 100^\circ \pm 2^\circ$.

bromide the first three were very intense in comparison with the rest, the fourth was perhaps slightly weaker than the fifth, which, in turn, was stronger than the sixth.

The dipole moment of phosphorus tri-iodide has been found by Malone and Ferguson¹⁰ to be zero, thus indicating the possibility of a planar molecule, but this structure appears to be ruled out by electron diffraction as the 120° model gives a theoretical intensity curve in which the third maximum is considerably weaker than the second and the fourth intermediate between the third and fifth in disagreement with the photographic plates. The model which gives a theoretical curve most closely in agreement with the plates appears to lie in the near neighbourhood of 100° . This is supported

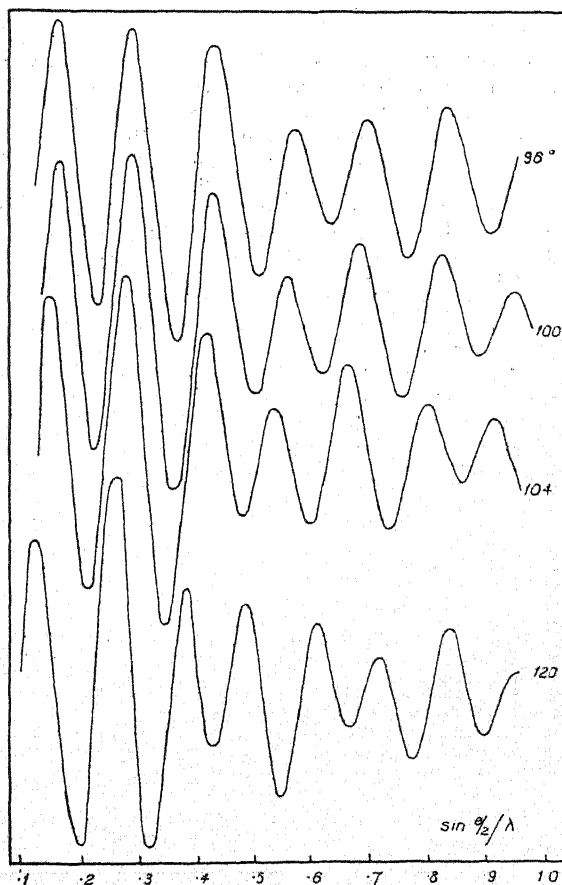


FIG. 6.—Scattering curves for phosphorus tri-iodide.

by the constancy of the phosphorus iodine distance (2.52 \AA.) calculated for 98° (Table VIII.). The curves were calculated taking $l_{\text{P-I}} = 2.40 \text{ \AA.}$

TABLE VIII.—PHOSPHORUS TRI-IODIDE.

Max.	No. of Measurements.	$\frac{\sin \theta/2}{\lambda}$ Exptl.	$(\sin \theta/2)/\lambda$.						$l_{\text{P-I}}$.					
			94°	98°	100°	102°	106°	120°	94°	98°	100°	102°	106°	120°
2	14	0.292	0.311	0.303	0.298	0.295	0.287	0.277	(2.56)	(2.49)	(2.45)	(2.42)	(2.36)	(2.28)
3	15	0.427	0.461	0.450	0.445	0.439	0.428	0.393	2.59	2.53	2.50	2.47	2.40	2.21
4	11	0.561	0.609	0.589	0.579	0.569	0.549	0.498	2.61	2.52	2.48	2.44	2.34	2.13
5	12	0.684	0.731	0.717	0.709	0.699	0.681	0.636	2.56	2.52	2.49	2.45	2.39	2.22
6	8	0.825	0.888	0.865	0.854	0.845	0.820	0.750	2.58	2.52	2.49	2.46	2.39	2.18
Average									2.59	2.52	2.49	2.45	2.38	2.18
Average deviation									0.012	0.002	0.005	0.01	0.02	0.03

Final results : $l_{\text{P-I}} = 2.52 \pm 0.01 \text{ \AA.}$; $\widehat{\text{I-P-I}} = 98 \pm 4^\circ$.

Arsenic Tribromide.—Eight visual maxima were obtained on all the plates taken with this substance. These consisted of a weak inner ring followed by a dense ridge which was in turn followed by a symmetrical but very intense maximum; a weak, but clearly visible, fourth maximum was spaced between this and a symmetrical strong fifth maximum. This was followed by a slightly less intense maximum, and then by a very diffuse one which was too indistinct to measure. A wide minimum then occurred followed by a weak but sharply defined eighth maximum. The minimum between the fifth and sixth rings was very pronounced. The characteristic weakness of the fourth ring immediately eliminates the 90° and 120° models whilst the symmetrical character of the third and fourth maxima rules out those for 96° and 110° . From the comparative data shown in Table IX (curves calculated for $l_{\text{As-Br}} = 2.50 \text{ \AA.}$), it will be seen that the position of the fourth ring relative to the third and fifth indicates that the 100° model is the most probable. As this model gives distances as calculated from each ring which differ least from the average as well as a sixth maximum less intense than the fifth and a very weak but somewhat diffuse seventh maximum it will be accepted as the most

TABLE IX.—ARSENIC TRIBROMIDE.

Max.	No. of Measurements.	$\frac{\sin \theta/2}{\lambda}$ Exptl.	$(\sin \theta/2)/\lambda$.						$l_{\text{As-Br}}$.					
			90°	96°	100°	102°	104°	110°	90°	96°	100°	102°	104°	110°
3	9	0.455	0.446	0.442	0.434	0.430	0.425	0.418	2.45	2.43	2.38	2.36	2.34	2.30
4	9	0.598	0.615	0.598	0.565	0.541	0.529	0.491	2.57	2.50	2.36	2.26	2.21	2.05
5	8	0.713	0.711	0.685	0.672	0.666	0.660	0.643	2.49	2.40	2.36	2.34	2.31	2.25
6	8	0.881	0.865	0.844	0.830	0.822	0.816	0.780	2.46	2.40	2.36	2.33	2.32	2.21
8	8	1.123	1.028	1.086	1.066	1.058	1.050	1.011	2.29	2.42	2.38	2.34	2.34	2.27
Average									2.45	2.43	2.37	2.33	2.30	2.22
Average deviation									0.07	0.03	0.01	0.02	0.04	0.07

Final results : $l_{\text{As-Br}} = 2.36 \pm 0.02$.

$\widehat{\text{Br-As-Br}} = 100^\circ \pm 2^\circ$.

suitable. The error of $\pm 2^\circ$ is based on the position of the fourth ring relative to the third and fifth. The corresponding Arsenic-Bromine distance is then 2.37 ± 0.1 .

Arsenic Tri-Iodide.—A sharply defined inner ring was just visible, being superimposed on a very intense ridge. This was followed by a third intense, symmetrical, and sharply defined ring; a weak, but easily visible fourth maximum lay between this and a well-defined symmetrical fifth maximum. The sixth maximum appeared as an equally well-defined, but weaker ring, beyond which could just be seen an ill-defined weak but definite maximum. On the edge of the plates an eighth well-defined symmetrical but weak maximum could just be measured.

Scattering curves for various angles, calculated for $l_{As-I} = 2.60$ Å., are shown in Fig. 8. The first two rings have been omitted as they are of no use in determining the structure. It will be seen that the 90° and 120° models are immediately eliminated by the characteristic weakness of the fourth ring. The 110° model is also ruled out as it requires a very weak sixth ring while on the plates this ring was only slightly weaker than the fifth. Of the remaining three models that for 100° seems the most suitable as it gives fifth and sixth rings of approximately correct intensity ratios, and, in addition, the seventh ring which could only just be seen on the plates is weaker than in either the 96° or 104° model. The quantitative data are given in Table X.; and it will be noticed that the observed position of the fourth ring relative to the third and fifth indicates that the most suitable model is an angle of 100° ; the error of $\pm 2^\circ$ is based on the definite inferiority of the 96° and 104° curves. The corresponding arsenic-iodine distance is 2.58 ± 0.1 Å.

Antimony Trichloride.—In antimony trichloride the antimony chlorine scattering is much stronger than that due to chlorine chlorine and change

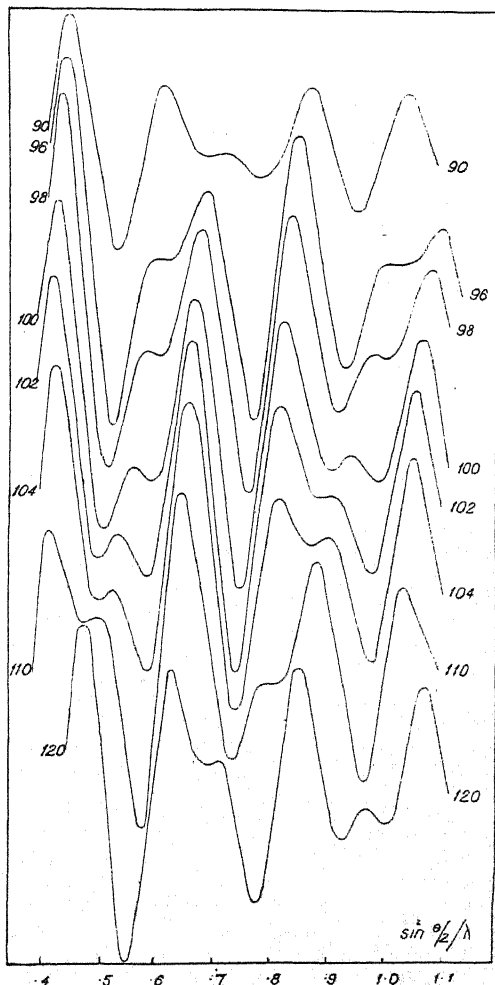


FIG. 7.—Scattering curves for arsenic tribromide. First two rings have been omitted as they are of no value in determining the structure.

in angle makes very little difference to either the scattering curves or the average value of the Sb—Cl distance as calculated from them.

The plates showed five symmetrical rings with no characteristic features, and the intensities of the rings decreased gradually towards the outside of the plate.

It seems probable that the angle will be in the neighbourhood of 100° , and it will be seen from Table XI. that an angle of 104° gives the values of the interatomic distance as calculated from each maximum which are most nearly constant.

A scattering curve for 104° and $l_{\text{Sb-Cl}} = 2.42 \text{ \AA}$. is shown in Fig. 9.

Antimony Tribromide.—The antimony tribromide plates showed five rings with only one distinguishing feature; the third maximum was a ridge with a very gradual rise in intensity on the inside edge and a very sharp outside edge, the other rings being quite symmetrical and gradually decreasing in intensity with increase in number of the ring. Examination of the scattering curves for various angles shown in Fig. 10

indicates that only in the neighbourhood of 96° does this characteristic

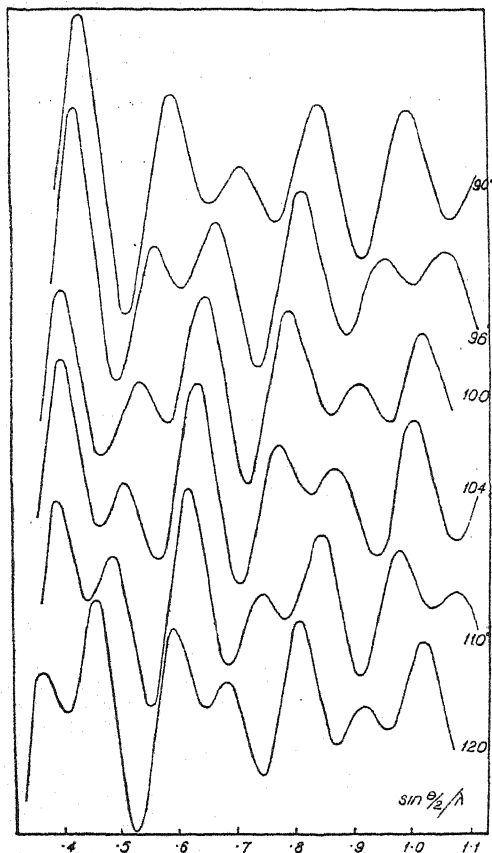


FIG. 8.—Scattering curves for arsenic tri-iodide, the first two rings have been omitted as they are of no value in determining the structure.

TABLE X.—ARSENIC TRI-IODIDE.

Max.	No. of Measurements.	$\sin \theta/2\lambda$ Exptl.	$(\sin \theta/2)/\lambda$						$l_{\text{As-I}}$					
			90°	96°	100°	104°	106°	110°	90°	96°	100°	104°	106°	110°
3	6	0.417	0.437	0.424	0.415	0.406	0.402	0.390	2.72	2.64	2.59	2.53	2.51	2.43
4	6	0.544	0.590	0.564	0.536	0.514	0.505	0.487	2.82	2.69	2.56	2.45	2.41	2.33
5	6	0.652	0.706	0.664	0.649	0.637	0.631	0.615	2.72	2.65	2.59	2.54	2.52	2.45
6	6	0.798	0.840	0.812	0.793	0.776	0.767	0.740	2.75	2.65	2.59	2.53	2.51	2.41
7	6	1.024	0.992	1.053	1.018	1.006	1.098	0.978	2.52	2.67	2.59	2.56	2.53	2.48
						Average	.	.	2.71	2.66	2.58	2.52	2.50	2.42
						Average deviation	.	.	0.07	0.02	0.01	0.03	0.03	0.04

Final result: $l_{\text{As-I}} = 2.58 \pm 0.01 \text{ \AA}$; $\angle \text{As-I} = 100^\circ \pm 2^\circ$.

ridge appear. It will be seen from Table XII. in which a quantitative comparison is given for all the models (calculated for $l_{\text{Sb-Br}} = 2.47$), that the 96° model shows the smallest average deviation. The average deviation for the 104° model is within the limits of experimental error, but this model requires a symmetrical third maximum. The estimated error of $\pm 2^\circ$ is based on the definite absence of a ridge in both the 90° and 100° models.

Antimony Triiodide.—The plates showed two dense inner rings followed by a ridge whose outer edge was quite sharp. The fourth maximum was also symmetrical and of approximately equal intensity with the third. Beyond this a very weak but apparently symmetrical fifth ring was visible. No evidence of an extra maximum between the fourth and fifth rings could be detected. The characteristic shape of the third maximum indicates immediately that the angle lies between 96° and 100° . As no maximum could be detected between the fourth and fifth rings the most suitable model appears to be 98° . This is supported by the quantitative data as shown in Table XIII. The curves were calculated for $l_{\text{Sb-I}} = 2.74 \text{ \AA}$.

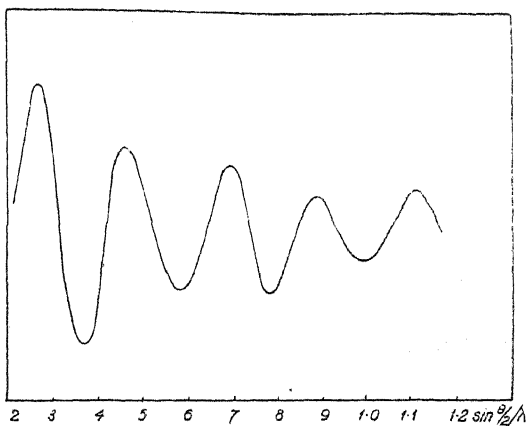


FIG. 9.—Scattering curve for antimony trichloride for 104° .

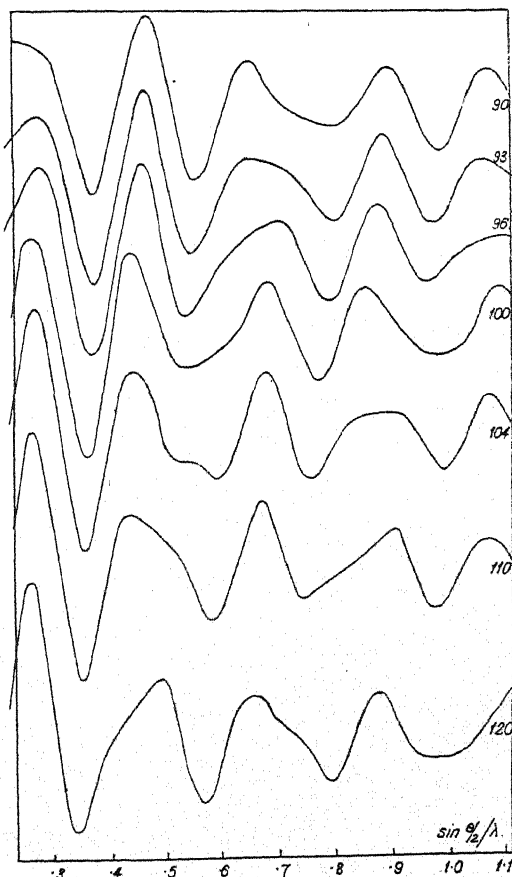


FIG. 10.—Scattering curves for antimony tribromide.

TABLE XI.—ANTIMONY TRICHLORIDE.

Max.	No. of Measurements.	$\frac{\sin \theta/2}{\lambda}$	$(\sin \theta/2)/\lambda$.						$l_{\text{Sb-Cl}}$					
		Exptl.	90°.	94°.	100°.	104°.	110°.	120°.	90°.	94°.	100°.	104°.	110°.	120°.
1	12	0.287	0.256	0.262	0.266	0.266	0.263	0.258	2.16	2.21	2.24	2.24	2.22	2.17
2	12	0.464	0.466	0.461	0.454	0.453	0.458	0.471	2.43	2.40	2.37	2.36	2.39	2.40
3	12	0.688	0.657	0.667	0.677	0.676	0.670	0.660	2.31	2.35	2.38	2.38	2.36	2.32
4	12	0.893	0.887	0.881	0.867	0.870	0.891	0.871	2.40	2.39	2.35	2.36	2.41	2.36
5	5	1.102	1.076	1.074	1.094	1.082	1.077	1.088	2.36	2.35	2.40	2.37	2.36	2.38
Average . . .									2.37	2.37	2.37	2.37	2.38	2.38
Average deviation									0.04	0.02	0.015	0.01	0.02	0.04

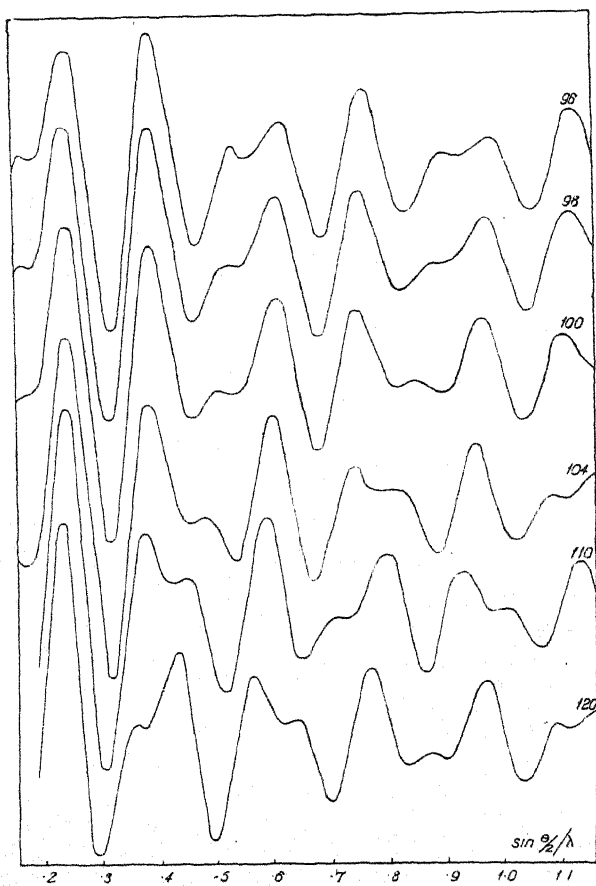
Final result : $l_{\text{Sb-Cl}} = 2.37 \pm 0.02 \text{ \AA.}$; $\text{Cl-Sb-Cl} = 104 \pm 5^\circ$.

FIG. 11.—Scattering curves for antimony tri-iodide.

TABLE XII.—ANTIMONY TRIBROMIDE.

Max.	No. of Measurements.	$\frac{\sin \theta/2}{\lambda}$ Exptl.	$(\sin \theta/2)/\lambda$.					$l_{\text{Sb-Br}}$				
			90°.	96°.	100°.	104°.	110°.	90°.	96°.	100°.	104°.	110°.
1	—	0.271	0.253	0.278	0.273	0.268	0.257	(2.30)	(2.53)	(2.49)	(2.44)	(2.34)
2	—	0.438	0.456	0.448	0.442	0.437	0.428	2.57	2.52	2.49	2.46	2.41
3	—	0.666	0.631	0.684	0.682	0.667	0.650	2.34	2.54	2.53	2.51	2.44
4	—	0.845	0.876	0.855	0.837	0.840	0.876	2.56	2.49	2.44	2.45	2.56
5	—	1.058	1.051	1.084	1.075	1.060	1.034	2.43	2.53	2.50	2.45	2.41
			Average . . .					2.47	2.52	2.49	2.47	2.45
			Average deviation					0.09	0.015	0.03	0.02	0.05

Final results : $l_{\text{Sb-Br}} = 2.52 \pm 0.02 \text{ \AA.}$; $\widehat{\text{Br-Sb-Br}} = 96 \pm 2^\circ$.

TABLE XIII.—ANTIMONY TRI-IODIDE.

Max.	No. of Rings Measured.	$\frac{\sin \theta/2}{\lambda}$ Exptl.	$(\sin \theta/2)/\lambda$.					$l_{\text{Sb-I}}$				
			96°.	98°.	100°.	104°.	110°.	96°.	98°.	100°.	104°.	110°.
2	12	0.397	0.400	0.398	0.394	0.388	0.380	2.76	2.75	2.72	2.68	2.62
3	12	0.613	0.628	0.618	0.613	0.603	0.587	2.81	2.76	2.74	2.69	2.62
4	12	0.765	0.774	0.764	0.756	0.741	0.795	2.77	2.74	2.71	2.65	2.84
5	4	0.976	0.991	0.981	0.972	0.955	0.931	2.78	2.76	2.73	2.68	2.62
6	3	1.125	1.134	1.126	1.114	1.114	1.142	2.76	2.74	2.71	2.71	2.77
			Average . . .					2.78	2.75	2.72	2.68	2.69
			Average deviation					0.016	0.008	0.01	0.017	0.11

Final results : $l_{\text{Sb-I}} = 2.75 \pm 0.02 \text{ \AA.}$; $\widehat{\text{I-Sb-I}} = 98 \pm 2^\circ$.

Summary.

Electron diffraction investigations have been made of the structures of phosphorus tribromide and tri-iodide, arsenic tri-bromide and tri-iodide, antimony trichloride, tribromide, and tri-iodide, mercuric chloride, bromide, and iodide, mercury dimethyl and boron trichloride.

The distance between the central atom and the attached atoms have been determined in all cases; the distances between attached atoms, or the covalency angles, have been determined in phosphorus tribromide and tri-iodide, arsenic tribromide and tri-iodide, antimony trichloride, tribromide, and tri-iodide, wherein the angles are all within a few degrees of 100° , and in mercuric iodide where it is $< 160^\circ$.

The results, combined with those of other workers, show that the interatomic distances in the fifth group iodides are equal to or greater than the sums of the Pauling-Huggins covalent radii: those of the bromides show a shortening of 1.2 per cent., those of the chlorides one of 2.4 per cent., and those of the fluorides 7-13 per cent. The mercuric halides, on the other hand, show greater shortening in the iodide than in the chloride, while boron appears to exhibit mixed behaviour.

It is suggested that there are at least two influences causing the observed shortenings: (1) the possibility, in mercury and boron, of resonance

of the ordinary structures with others in which the octet is completed by formation of co-ordinate links from a halogen atom to the central atom, (2) the polar character of the bonds, which may either be the direct cause or the indirect cause by permitting double-bonded structures without increase of the octet on the central atom.

It is shown that the constancy of the valency angles in the fifth group trihalides may possibly be due to complicated compensations of several opposing tendencies, but doubt is expressed of the adequacy of this explanation.

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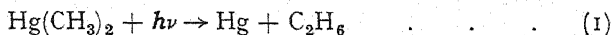
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THE PHOTOCHEMISTRY OF POLYATOMIC MOLECULES CONTAINING ALKYL RADICALS. VI. PHOTOLYSIS OF MERCURY DIMETHYL.

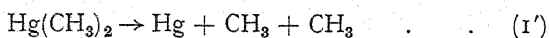
BY H. W. THOMPSON AND J. W. LINNETT.

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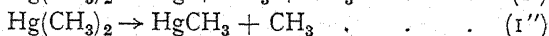
In Part IV. of the present series,¹ measurements on the photochemical decomposition of mercury dimethyl under the influence of ultra-violet light (2537 Å.) were described. The products are metallic mercury and a mixture of hydrocarbons of which ethane is by far the most predominant. The quantum efficiency of the decomposition at room temperatures was found to be unity within the limits of experimental error. The facts could be well explained by the hypothesis that the primary act is



without the production of reaction chains, but it was suggested that simultaneously a few free radicals produced by one or both of the processes:



and



may give rise to chain-propagation and to subsidiary hydrocarbon products.

The present paper describes further measurements on this reaction,

¹ *Trans. Faraday Soc.*, 1937, **33**, 501.

and falls into two separate sections, (1) the study of the photolysis at higher temperatures, (2) the examination of the effect of nitric oxide on the reaction. It was thought likely that if chains are at all appreciably propagated in the photolysis, this effect should become more marked at higher temperatures and lead to a higher overall quantum efficiency. Again, the ability of small traces of nitric oxide to retard the decomposition of certain ethers and other organic molecules,² has recently been attributed to the breaking of reaction chains by the nitric oxide, presumably by interaction with free alkyl radicals. It was thought possible that free radicals might be detected in the present decomposition by this method, although it is to be remembered that at room temperature the effect might be less marked than at higher ones. If in reality the reaction proceeds to a great extent through the propagation of reaction chains, and the quantum efficiency is reduced to roughly unity by virtue of an inefficient primary process, this should be detectable from the effect of nitric oxide.

Experimental Method.

The apparatus and procedure were essentially as previously described. The quartz reaction cell, cylindrical in shape, was wound with resistance wire and suitably lagged, so that the vessel could be heated to 400° C. or less as required. It was impracticable to obtain complete uniformity of temperature within the cell, especially near the end faces, but no serious errors were introduced as a result of this, and the conclusions drawn from the experimental data are not materially affected by it. The apparatus shown in Fig. 2 of the previous paper was modified by the introduction of a narrow U-tube between the cell and the tap through which the whole system was evacuated. The tube served as a freezing-out trap instead of the cell itself as in the previous series of experiments. For the runs at high temperatures the procedure was as follows. Mercury dimethyl was first introduced at room temperatures into the cell to the desired pressure, which was recorded on the oil manometer. The cell was then heated and when at a steady temperature, the pressure of mercury dimethyl was measured on the mercury manometer. The pressure increase over the heating-up period gave a check on the temperature of the cell. The vapour was then irradiated and after a known interval the cell was allowed to cool to room temperatures, after which the pressure was remeasured on the oil manometer. It was always found to be the same as the initial pressure, *i.e.*, the reaction proceeds without pressure change. The U-tube was then cooled in a mixture of acetone and solid carbon dioxide and the contents of the cell drawn through it slowly. The freezing mixture around the U-tube was then removed and the pressure of the residual mercury dimethyl measured at room temperature, thus obtaining by difference the amount of mercury dimethyl which had disappeared. A blank experiment with no illumination showed that even at the highest temperatures used (*ca.* 200° C.) there was no appreciable thermal decomposition of the mercury dimethyl. The radiation used was the 2537 Å. line of a hot mercury arc, and the quantum yield was determined by the actinometric method previously described.

Pure nitric oxide was prepared by the action of a solution of potassium nitrite in concentrated sulphuric acid on mercury in a gas-holder, the gas being stored over the mercury and the holder leading through a spray trap of glass wool to the cell. In determining the quantum efficiency of the disappearance of mercury dimethyl the following pressures were measured ;

² Staveley and Hinshelwood, *Nature*, 1936, **137**, 29 ; *Proc. Roy. Soc., A*, 1936, **154**, 335 ; *J.C.S.*, 1936, 812, 818 ; *Proc. Roy. Soc., A*, 1937, **159**, 192 ; Mitchell and Hinshelwood, *ibid.*, 1937, **159**, 32.

the pressure of mercury dimethyl introduced, the total pressure of mercury dimethyl and nitric oxide before illumination, the total pressure after illumination, and the pressure of mercury dimethyl remaining after removal of nitric oxide and other volatile products by the method described above. The amount of mercury dimethyl which had disappeared could then be deduced.

Results.

(1) Photolysis of Mercury Dimethyl at Higher Temperatures.

The absence of pressure change in the photochemical decomposition at the higher temperatures is an indication that there is no essential difference in the products formed from those previously found at lower temperatures.

In Table I. the results of several runs at different temperatures are summarised :—

TABLE I.—EXPOSURE IN EACH RUN 40 MINS.

Run.	Initial Press. at Room Temp. mm.	Room Temp. ° Abs.	Press. after Heating up. mm.	Cell Temp. ° Abs.	Gm. Mols. $\text{Hg}(\text{CH}_3)_2 \times 10^5$ Decomposed.	Gm. Mol. Quanta $\times 10^5$.	γ .
1	15.2	290	20.4	389	2.42	1.39	1.74
2	15.4	290.5	21.2	400	2.32	1.49	1.56
3	13.5	290	21.5	462	2.56	1.16	2.21
4	13.65	286	21.15	422	2.43	1.28	1.90
5	16.0	—	—	—	2.62	1.81	1.45

It is seen that with rising temperature the quantum yield increases. This is presumably due to the more favourable conditions for the propagation of chains.

(2) The Influence of Nitric Oxide at Room Temperatures.

When mercury dimethyl vapour and nitric oxide are irradiated at room temperature with ultra-violet light, a white solid deposit is formed on the vessel walls, and mainly on the front (incident) face. The formation of the deposit is accompanied by a marked decrease in pressure and the deposition on the front face leads to a slightly diminishing intensity of the radiation entering the cell. In determining the quantum yield, three measurements of light transmitted through the cell were made: (1) with the clean cell evacuated before the run, (2) during the entire run, (3) with the cell evacuated after the run. The light absorbed by the mercury dimethyl vapour was taken to be the difference between

TABLE II.—PRESSURE OF NITRIC OXIDE 8.5 mm. TEMPERATURE 17° C. PRESSURE OF MERCURY DIMETHYL 22.5 mm.

t (mins.).	Total Pressure Reading.	t (mins.).	Total Pressure Reading.
0	31.0	54	22.0
13	31.0	57	21.0
24	31.0	60	20.5
26 *	31.0	66	20.0
29	31.0	72	20.0
33	30.0	77	20.0
36	29.0	82	20.5
39	28.0	90	21.0
41	27.0	94	21.0
43	26.0	102	21.0
46	25.0	110 †	21.0
49	24.0	124	20.5
51	23.0		

* Light on.

† Light off.

(2) and the mean of (1) and (3). Since (3) was only some 10 per cent.

lower than (1) the errors involved in this procedure cannot be large, and it seems the most satisfactory. Owing to the minute amounts of the solid deposit formed it has not so far been possible to determine its chemical composition. The formation of the solid product and the accompanying pressure decrease are observed regardless of the relative proportions of mercury dimethyl and nitric oxide initially introduced.

It is clear that in the presence of nitric oxide the photochemical reaction follows a completely different course from that observed in the absence of nitric oxide. The possibility of photosensitisation by nitric oxide can of course be neglected, since this substance does not absorb the frequency of the light used. Table II. gives measurements of pressure during the course of a run. It was found that taking roughly equal initial pressures of mercury dimethyl and nitric oxide the initial decrease of pressure ceased abruptly after a certain interval, although at this point mercury dimethyl still remains, and although further illumination caused no further pressure change, nevertheless further photochemical decomposition of this residual mercury dimethyl occurred.

TABLE III.

Initial Press. Hg(CH ₃) ₂ mm.	Final Press. Hg(CH ₃) ₂ mm.	Initial Press. No. mm.	Quanta Absorbed × 10 ⁶ .	γ.
15.0	12.0	10.65	1.09	1.1
14.2	11.1	9.6	1.38	0.9
12.85	8.9	12.25	1.18	1.1
15.2	10.8	14.1	1.50	1.1
12.2	9.7	17.2	1.37	0.8
21.1	18.2	1.6	1.48	0.8
19.1	14.4	0.5	1.46	1.2
16.9	13.8	2.0	1.34	0.9

The reaction involved during the pressure decrease has a quantum efficiency of unity within experimental error. This is indicated by the data of Table III.

(3) The Influence of Nitric Oxide at Higher Temperatures.

The photolysis of mercury dimethyl in the presence of nitric oxide at higher temperatures is much more complicated than at the lower temperatures described above. Gaseous products are formed in addition to the solid deposit, and the reaction seemed unsuitable for detailed study.

Discussion.

In the light of the new data, and particularly the markedly increased value of the quantum yield at higher temperatures, it is now desirable to revise the suggestions previously made (formulæ 1, 1' and 1'') for the mechanism of the photolysis of mercury dimethyl. On the basis of Terenin's value for the energy of the Hg-C link,³ process (1') would appear to require a greater energy than is provided by the quantum absorbed. On the basis of the following mechanism, which incorporates all plausible elementary processes, it seems possible to interpret all the previous data and also the measurements just described, both at higher temperatures and in the presence of nitric oxide. Further, interesting results are thereby deduced in regard to the kinetics of the several individual elementary processes.

³ *C.r. Acad. Sci. U.S.S.R.*, 1935, 1, 482; *Acta Physico chim. U.S.S.R.*, 1935, 1, 759; *J. Chem. Physico*, 1934, 2, 441.

The scheme suggested is the following :—

- (1) $\text{HgCH}_3 + h\nu \rightarrow \text{HgCH}_3 + \text{CH}_3$
- (2) $\text{HgCH}_3 + x \rightarrow \text{Hg} + \text{CH}_3$
- (3) $\text{HgCH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{Hg} + \text{C}_2\text{H}_6 + \text{HgCH}_3$
- (4) $\text{CH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{HgCH}_3 + \text{C}_2\text{H}_6$
- (5) $\text{CH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{Hg} + \text{CH}_3 + \text{C}_2\text{H}_6$
- (6) $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$
- (7) $\text{CH}_3 + \text{HgCH}_3 \rightarrow \text{Hg} + \text{C}_2\text{H}_6$
- (8) $\text{HgCH}_3 + \text{HgCH}_3 \rightarrow 2\text{Hg} + \text{C}_2\text{H}_6$

In this scheme, (3), (4) and (5) are the chain propagating stages, and in order that the reaction shall have a quantum yield of unity as regards disappearance of mercury dimethyl, it is necessary to assume that stages (3), (4) and (5) involve a high energy of activation. It can be seen that a combination of (1), (2) and (6) or of (1), (6), (7) and (8) will give $\gamma = 1$. At higher temperatures the acquisition of the energy of activation required for processes (3), (4) and (5) will lead to chain propagation and γ will rise above unity. It is possible from the measurements at room temperatures to make an estimate of the minimum energy of activation for processes (3), (4) and (5).

Taking data from the previous paper (p. 505), with an initial pressure of mercury dimethyl of *ca.* .20 mm., the light absorbed in 40 minutes was about 1.37×10^{-5} gm. mol. quanta, *i.e.*, about 5×10^{13} quanta per c.c. per second. In accordance therefore with stage (1) the number of free radicals (CH_3 or HgCH_3) produced per c.c. per second is 10×10^{13} . For a steady state this will be equal to the number which disappear. Suppose that each of the processes (6), (7) and (8), by which the radicals disappear, has zero energy of activation, and for the radicals CH_3 and HgCH_3 take a mean radius of 5×10^{-8} cm. Similarly for these two radicals assume a mean value of the root mean square velocity of $\bar{u} = 5 \times 10^4$ cm./sec. Then the number of collisions per c.c. per second between pairs of free radicals is $\sqrt{2\pi}\bar{u}\sigma^2n^2$ where n is the concentration of free radicals in radicals per c.c. Writing $\sqrt{2\pi}\bar{u}\sigma^2n^2 = 10 \times 10^{13}$, we have $n = 4.2 \times 10^{11}$ radicals per c.c. At a pressure of 10 mm. (the mean during the run), and at 17° C., the concentration of mercury dimethyl is 3.4×10^{17} molecules per c.c. Thus a free radical will in general meet a molecule of mercury dimethyl 10^6 times more frequently than it meets another free radical.

Now if the energy of activation of processes (3), (4) and (5) was zero, the quantum yield would be of the order 10^6 . Actually it is only of the order unity. If the probability of a collision of a free radical with a mercury dimethyl molecule being an effective one were 10^{-6} , then the quantum yield would be roughly two. Thus collisions between free radicals must result in interaction even less frequently than 1 in 10^6 . If the probability of interaction were 1 in 10^8 , the quantum yield would be about 1.01. A probability of 1 in 10^7 would give $\gamma = 1.1$. The latter value differs from unity by an amount which would probably have been detected. We can therefore write

$$10^{-8} = e^{-E/RT} = e^{-E/580},$$

whence $E = 10,700$ cal.

If the probability of interaction is $< 10^{-8}$, E will be correspondingly higher, and under these circumstances γ will be even closer to unity.

The inference is therefore that for the reaction between free radicals and mercury dimethyl molecules the energy of activation is at least 10,700 cal.

The measurements of quantum yield at the higher temperatures make it possible to make an independent estimate of this energy of activation. If for a given initial pressure of mercury dimethyl at a given temperature the concentration is c_1 molecules per c.c., and the number of free radicals per c.c. in the steady state, calculated as before, is c_2 , and the quantum yield is $(1 + x)$, then

$$\frac{c_2}{c_1} \times x = e^{-E/RT}.$$

This equation shows how with increasing quantum yield, E must decrease. Using the equation, and applying the data given in Table I., the values deduced for E for four runs are 10,900, 11,400, 12,400, and 11,600, giving a mean of 11,600 cal. This agrees very well with the value previously calculated, although the former value was only regarded as a rough minimum. It is interesting to compare the value found with those suggested for other similar elementary processes, *e.g.*, for the interaction of methyl radicals with acetaldehyde molecules the value suggested by Leermakers⁴ and by Hinshelwood² is about 9000-10,000 cal.

Although the photochemical reaction which takes place when mercury dimethyl is illuminated at room temperatures in the presence of nitric oxide is very complicated, the quantum efficiency in terms of disappearance of mercury dimethyl is still close to unity. This result makes it certain that the quantum yield of the primary process is really unity and is understandable if the nitric oxide reacts only with the free radicals formed by the primary process. If we assume that the nitric oxide and radicals interact to give only a solid product, as the experimental work suggests, it is possible to determine the proportions of nitric oxide and mercury dimethyl molecules disappearing. The following table shows that this ratio is always about 2:—

Before Illumination.		After Illumination.		Hg(CH ₃) ₂ Used mm.	NO Used mm.	Ratio.
Hg(CH ₃) ₂ mm.	Hg(CH ₃) ₂ + NO mm.	Total mm.	Hg(CH ₃) ₂ mm.			
18.0	29.35	17.0	13.9	4.1	8.25	2.01
14.05	26.35	15.7	10.45	3.6	7.05	1.96
14.1	28.6	13.6	9.1	5.0	10.0	2.00
12.85	25.1	12.45	8.9	3.95	8.70	2.2
15.2	29.3	16.5	10.8	4.4	8.4	1.91
12.2	29.4	19.0	9.7	3.5	6.9	1.97

This suggests that perhaps one free radical reacts with each molecule of nitric oxide. The nature of these reactions can only be imagined, but one possibility is that methyl radicals unite with nitric oxide to form CH₃NO, which isomerises to give CH₂NOH, the oxime of formaldehyde. The latter may well appear as a solid polymer. At higher temperatures this substance would be unstable and might be supposed to decompose

⁴ *J. Am. C. S.*, 1934, 56, 1537.

into CO and NH_3 . Evidence for the production of ammonia in the inhibition by added nitric oxide of ether decompositions will shortly be described in another paper.

The attempts to study the photolysis in the presence of nitric oxide at higher temperatures may well have been frustrated by the decomposition of the solid product just referred to, or by the formation of gaseous products in the reaction between the radicals and the nitric oxide molecules.

Finally, it may be pointed out that a precisely similar mechanism to the one given above, may be applied to the data of Leighton and Mortensen⁵ on the photolysis of lead tetramethyl, and gives a good interpretation of their data. Since the quantum yield measured by them is higher than in the present reaction, we should infer that the energy of activation of the reaction of methyl radicals with lead tetramethyl molecules is lower than 10,000 cal. Leighton and Mortensen also found that in the presence of oxygen the quantum yield was reduced to unity. This may well have arisen by the stoppage of chain propagation by a reaction of the oxygen with methyl radicals. The mechanism used above is also in accordance with the ideas of Terenin⁶ on the primary process in the photo-decomposition of mercury dimethyl.

Summary.

Measurements on the photolysis of mercury dimethyl vapour by ultra-violet light have been extended. The decomposition has been studied at higher temperatures, and also in the presence of nitric oxide. At the higher temperatures the quantum yield, which is unity at room temperatures, rises to greater values. In the presence of nitric oxide, a solid product is formed, but the quantum yield of the disappearance of mercury dimethyl is still unity. All the facts are well explained on the basis of a scheme of elementary processes, and an estimate of the energy of activation of the reaction of a methyl radical with metal alkyl molecules suggests about 11,000 cal. It appears that perhaps one free radical disappears for each molecule of nitric oxide in the presence of the latter substance, and suggestions are given to account for this.

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⁵ *J. Am. C. S.*, 1936, 58, 448.

⁶ *Trans. Faraday Soc.*, 1935, 31, 1483.

THE DETERMINATION OF THE CARBOXYLIC ACID GROUP IN OXYCELLULOSES.

BY S. M. NEALE AND W. A. STRINGFELLOW.

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Introductory.

Although oxidation always reduces the viscosity and tensile strength of cellulose, the chemical nature of the products formed when cellulose is treated with oxidising agents depends upon the conditions of oxidation.¹ "Oxycelluloses" prepared in neutral or acid solution are able, in general, to reduce alkaline copper solutions, and do not absorb basic dyes, such as Methylene Blue, much more strongly than unoxidised cellulose. In alkaline media, on the other hand, substances are obtained which have low copper numbers and an increased absorptive value for basic dyes; they absorb direct cotton dyestuffs, such as Sky Blue FF, less strongly, however, than does unmodified cellulose.

The increased absorption of Methylene Blue has been successfully employed by Clibbens and co-workers² as a quantitative index of the state of oxidation of the material. The absorption varies so largely with the p_H , however, that the test in its present form cannot be used to determine the carboxylic acid group to which presumably the increase is due.

The effect of alkaline oxidation in reducing the absorption of the direct cotton dyestuff Sky Blue FF, has already been examined by the present authors.³ It was shown that the absorption of Sky Blue FF by cellulose, from solutions containing sodium chloride, could be explained quantitatively by applying the principle of the Donnan equilibrium, and that the decreased dye absorption found for certain oxycelluloses could be attributed to the presence of carboxylic acid groups, which entered into ionic equilibria with the solution. If an oxycellulose of this acidic type is placed in sodium chloride solution, the solution shows an acid reaction⁴ since a certain proportion of the hydrogen ions arising from the carboxylic acid groups are replaced by sodium ions and are thus enabled to escape from the cellulose phase, and to distribute themselves throughout the two phases in accordance with the principle of membrane equilibrium:—

Cellulose Phase.	Solution Phase.	Cellulose Phase.	Solution Phase.
(1)	(2)	(1)	(2)
—COOH	Na ⁺	—COOH	Na ⁺
—COO ⁻	Cl ⁻	—COO ⁻	H ⁺
H ⁺		H ⁺	Cl ⁻
		Na ⁺	
		Cl ⁻	
<i>Initial</i>		<i>Final</i>	

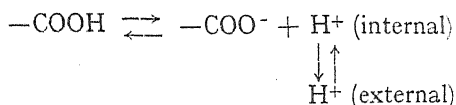
¹ Birtwell, Clibbens and Ridge, *J. Text. Inst.*, 1925, **16**, 15T.

² *Ibid.*, 1923, **14**, 297T; Clibbens and Geake, *J. Text. Inst.*, 1926, **17**, 141T.

³ Hanson, Neale and Stringfellow, *Trans. Faraday Soc.*, 1935, **31**, 1718.

⁴ Neale, *Nature*, 1935, **135**, 583; Schwalbe and Becker, *Ber.*, 1921, **54**, 545.

On adding alkali to the system, the equilibrium



is displaced towards increasing $-\text{COO}^-$ concentration, until all the $-\text{COOH}$ groups have been neutralised.

The present paper describes attempts to titrate carboxylic acid groups in cellulose, utilising this mobilisation of the hydrogen ions in the presence of a neutral electrolyte such as sodium chloride. Before such a titration can be carried out with an oxycellulose it is evidently essential to wash the material thoroughly free from cations, in order that the whole of the carboxylic acid may be originally present as such, and not partly in the form of salts. In the work described in this paper this was done by first leaving the oxycellulose for half an hour in cold 2N hydrochloric acid, and then washing repeatedly with distilled water, until the washings were neutral to brom-cresol-purple (p_H 5.2-6.8). For highly oxidised specimens, which are apt to give rise during washing to very fine debris, it is necessary to filter the washings before testing for neutrality, as the suspended fine matter itself shows an acid reaction with the indicator.

To test the efficacy of the washing process the ash alkalinities of several of the washed samples were determined, in duplicate, by the method described by Birtwell, Clibbens and Ridge.¹ The results are given in the Table. It will be seen that they are of the same order as those found for unoxidised cotton; whatever variation they show does not appear to bear any relation to the carboxylic acid value.

Electrodialysis might be expected to afford a more certain method of removing cations. Although more rapid, it has not been found, however, to be any better in the long run, judging by its effect upon carboxylic acid titre, which was not appreciably altered by prolonged electrodialysis. Ash alkalinities of dialysed samples were not determined.

Schmidt⁵ claims to have determined the acidity of unmodified cellulose by direct titration with alkali, but without adding sodium chloride. He employed both indicator and conductimetric methods of titration. Later in the present paper are described some unsuccessful attempts to confirm his results and also those obtained by Lüttke,⁶ who carried out titrations of cellulose with alkali in the presence of excess calcium acetate. Experiments are also described in which the p_H values of sodium chloride solutions in contact with oxycelluloses were determined, with a view to calculating an ionisation constant for the carboxylic acid groups.

The method given in this paper for determining carboxyl groups by back titration has already been referred to, with due acknowledgments, in a paper by Nabar, Scholefield and Turner⁷ who have used it in work carried out in the same Institute upon the oxidation of cellulose by hypochlorite.

⁵ E. Schmidt and others, *Ber.*, 1934, **67**, 2037.

⁶ Lüttke, *Papier Fabrikant*, 1934, **32**, 509, 528; *Angew. Chem.*, 1935, **48**, 650.

⁷ Nabar, Scholefield and Turner, *J. Soc. Dyers and Colourists*, 1937, **53**, 5.

Experimental.

Preliminary experiments showed that it was impossible to obtain a satisfactory end-point with a titration carried out directly in the manner suggested. The end-point drifted over a period of several hours. It was thought that this might be due to the presence of rather stable lactone groups, which reverted only slowly to the carboxylic acid form. To test this possibility, some titrations were carried out after various treatments—such as increased initial H^+ ion concentration or previous vacuum drying of the sample—which might be expected to favour lactone formation. The results suggested, though not very conclusively, that the "lactone theory" was correct.

A more satisfactory end-point was obtained by first adding an excess of dilute sodium hydroxide to the sodium chloride solution containing the oxycellulose and then titrating back with dilute hydrochloric acid. Gluconic acid, which easily gives rise to a lactone, behaved on titration similarly to the oxycelluloses.

In this preliminary work CO_2 -free air was passed through the solution and the latter kept boiling during the whole of the experiment. Fairly reproducible results could be obtained by this method with oxycelluloses of the non-reducing type, prepared by alkaline oxidation.

It is known, however, that oxycelluloses of the reducing type may partially dissolve on treatment with hot alkalis, and it has been suggested that this may involve the formation of soluble carboxylic products. As oxycelluloses in general are of a mixed type—even the acidic, so-called "non-reducing" ones having usually a somewhat higher copper number than unoxidised cellulose—the estimation of carboxyl groups under these conditions might be expected to give results which are too high.

It appeared desirable, therefore, in determining carboxylic acid groups, to avoid heating the solutions, except for a brief period near the end of the titration, when it is necessary to boil in order to expel carbon dioxide. The procedure finally adopted was therefore as follows:—

Place 1 gram (dry wt.) of the sample, cut up into small pieces, in a hard-glass 250 c.c. stoppered conical flask. If the sample is not already free from cations, wash with hydrochloric acid and distilled water until neutral, as described in the introductory section.

Then add 20 c.c. of 50 gm./litre sodium chloride solution, and 20 c.c. of $N/50$ sodium hydroxide. Allow to stand, with flask stoppered, for half an hour in the cold, then add four drops of brom-cresol-purple indicator solution, and titrate with $N/50$ hydrochloric acid, boiling and passing CO_2 -free air into the flask towards the end of the titration only.

With such precautions, results were obtained which, for a given oxycellulose, agreed within a few per cent. It was found that these were unaffected by increasing the time of standing in the cold up to 20 hours. Blank experiments, under the same conditions, but without cellulose present, showed that the latter only was concerned in producing the acidity measured.

The method has so far been used only for oxycellulose of the non-reducing type. It appeared to work satisfactorily when applied to determining the presumably quite low $-COOH$ values of several typical hydrocelluloses—strongly reducing products obtained from cellulose by acid hydrolysis. Thus, by the above "cold titration" method, a hydrocellulose of copper number 3.46 gave a $-COOH$ value of about 0.5 milliequivalents per 100 grams of the sample, even after standing 20 hours in the alkaline solution. By the earlier boiling technique a stable end-point could not be obtained, the alkali titre rising continuously to a value far higher than could be reasonably anticipated for such material. It cannot be assumed, however, that reducing oxy-celluloses would behave similarly to hydrocelluloses in this respect, and it is proposed to carry out further experiments with oxycelluloses of high copper number.

Preparation of Oxycelluloses.

As experimental material a number of samples of oxycellulose were prepared under various conditions of oxidation, which are set forth in detail in Table I. Most of them were made by the action of alkaline

TABLE I.*

Oxycellulose Sample Number.	Prepared From.	Oxidising Medium.	Wt. of Cotton in gms./1000 c.c. of Oxidising Soln.	Oxygen Consumption (Milli-atoms per 100 gms. Cellulose).	—COOH Value found (Milli-equivs. per 100 gms. Cellulose).	Copper Number, (Gms. per 100 gms. Cellulose.)	Ash Alkalinity Milliequivs. per 100 gms. Cellulose.	Fluidity in 2 Per Cent. Solution.	Remarks.
Unoxidised standard cotton cloth					Using NaCl/BaCl ₂ 0.2	0.04	0.54 (yarn)	4.4 in 0.5 % soln.	
1	Cotton cloth.	BrO = M/400 OH = N/10	25	10.0	1.9	1.7	0.41	3.6	
2	"	Oxygen in presence of NaOH.		17.2	2.20				
3	"	BrO = M/200 OH = N/10	25	20.0	3.70	3.4	0.55	6.0	
4	Cotton yarn.	" = " " = "	25	20.0	3.10				
5	Cotton cloth.	" = M/100 " = N/10	25	40.0	8.4	8.4	0.67		
6	Cotton yarn.	" = M/100 " = N/10	25	40.0	7.6				
7	Cotton cloth.	" = M/400 " = N/10	5	50.0	6.3	0.61	0.67	11.1	} Slow oxidation
8	Cotton cloth.	" = M/400 " = N/10	5	50.0	6.3			12.9	
9	Mercerised cloth.	" = M/400 " = N/10	5	50.0	8.2	0.84			
10	Cotton cloth.	KMnO ₄ = 0.008M. Na ₂ CO ₃ = 1.0N.	24	50.0	11.2				
11	Cotton cloth.	BrO = M/20 OH = N/10	25	52.0	11.0		1.69	11.0	} Rapid oxidation.
12	Cotton cloth.	" = M/40 " = N/10	25	100.0	20.0	0.89	0.81	18.1	

* For the hypobromite oxidations, conditions were so arranged that the reaction proceeded until the solution was completely exhausted in oxidising strength, except in the case of oxycellulose No. 11, when it was stopped at about one quarter exhaustion. Copper numbers were determined by the Schwalbe-Braidy method as modified by Heyes.⁹

hypobromite solution⁸ upon bleached cotton cloth of high quality (Tootal Broadhurst, Lee and Company's "Standard Tarantulle"; Copper No. 0.04, Fluidity in 0.5 per cent. soln., 4.4). The cloth, cut into pieces about an inch square, was shaken with a known volume of solution of determined strength until the desired quantity of oxygen had been consumed. By a suitable choice of concentration and of the ratio weight of cellulose/volume

⁸ Birtwell, Clibbens, Geake and Ridge, *Shirley Institute Memoirs*, 1929, 8, 155; *J. Text. Inst.*, 1930, 21, 85T.

⁹ Heyes, *J. Soc. Chem. Ind.*, 1928, 47, 90T.

of solution, both the final extent of oxidation and the rate at which it occurred could be controlled. It was shown by blank experiments in the absence of cotton that the hypobromite solutions did not lose strength appreciably through spontaneous decomposition over similar periods.

For one sample (No. 10 in Table I.) alkaline permanganate was used as oxidant; another (No. 2) was prepared after the method of Davidson¹⁰ by the action of oxygen in presence of sodium hydroxide, the extent of oxidation being indicated by the volume of gaseous oxygen consumed. Mercerised cloth was used for one preparation (No. 9) instead of Standard Tarantulle. It was prepared from the latter by treating for ten minutes with 5*N* sodium hydroxide, and was washed free of alkali, but not dried, before being immersed in an alkaline hypobromite solution for oxidation.

Before being used for carboxylic acid determination the oxycelluloses were washed thoroughly to remove cations, as described in the introductory section. The $-\text{COOH}$ values were calculated on a dry-weight basis, allowance being made for moisture regain in weighing samples for titration.

The figures given represent in each case the mean of two or more determinations.

The variation of $-\text{COOH}$ value with oxygen consumption is shown graphically in Fig. 1.

With hypobromite as oxidising agent it will be seen that:

(a) Under more or less comparable conditions of oxidation—i.e., with a constant ratio of 25 gms. of cotton to 1000 c.c. of solution—there is a fairly good linear relation between the two quantities over the range investigated, about five atoms of oxygen being required for the production of one carboxylic acid group. Nabar, Scholefield and Turner⁷ found a

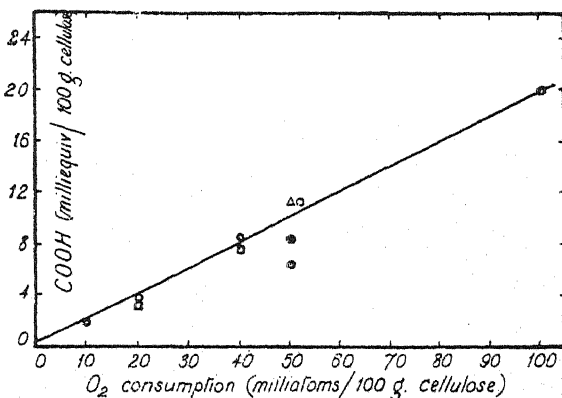


FIG. 1.—Relation between oxygen consumption and carboxylic acid titre.

- Cotton cloth oxidised by alkaline hypobromite.
- Cotton yarn oxidised by alkaline hypobromite.
- △ Cotton cloth oxidised by alkaline permanganate.
- Cotton cloth, mercerised, oxidised by hypobromite.

similar linear relationship in the case of cellulose oxidised by hypochlorite in the presence of a reduced vat dye, which greatly increased the rate of oxidation. With such material, however, the ratio of oxygen consumption to carboxyl produced was about 1.4 times as great, but this is quantitatively explained by them in terms of the increased proportion of aldehyde groups in their oxycelluloses. As these authors point out, the relatively large consumption of oxygen is consistent with the behaviour of the simple sugars, which generally undergo fission of the molecule with consequently high oxygen consumption when oxidised in alkaline solution.

¹⁰ Davidson, *Shirley Institute Memoirs*, 1932, 11, 21; *J. Text. Inst.*, 1932, 23, 95T.

(b) Increasing the rate of oxidation (in the case of oxycellulose No. 11) had little, if any, effect on the —COOH value for a given oxygen consumption.

(c) Decreasing the rate of oxidation (5 gms. of cellulose per 100 c.c. caused a marked fall in —COOH value.

(d) For the same ratio of cotton to solution and the same oxygen consumption, mercerised cotton gave rise to a product of higher —COOH content.

(e) There was, as might be expected, little difference between the results obtained with bleached standard cloth and bleached yarn of similar quality (Cu No. 0.02, fluidity in 0.5 per cent. soln., 4.2). The yarn used showed a slightly lower —COOH value than the cloth, especially at low oxygen consumption. This may be due, however, to the fact that the yarn, which had not been ammonia-washed to remove traces of fatty acids, contained impurities which themselves used up some of the oxygen.

The —COOH values found for the unoxidised cloth, and for a sample of unoxidised yarn which *had* been washed in hot dilute ammonia solution prior to removal of cations, were both about 0.2 milli-equivalents per 100 gms., but owing to the small titres involved it was difficult to decide whether there was any appreciable difference between them.

For Oxycelluloses 1, 3, and 5, titrations were also carried out in which barium chloride solutions of equivalent strength were used in place of sodium chloride. The results, which do not differ greatly from those obtained with the latter salt, are included in Table I.

The fluidities of 2 per cent. solutions of several of the oxycelluloses in cuprammonium were determined by the standard method, and are given in Table I. It will be seen that, on the whole, the fluidity rises with increasing degree of oxidation.

Comparative measurements of Methylene Blue absorption were not undertaken. As Methylene Blue absorption depends upon the p_H of the dye solution, such a comparison with —COOH values could only be carried out under arbitrarily chosen conditions. Moreover, as Birtwell, Clibbens and Ridge¹ point out, "it is certain that the determination of Methylene Blue absorption of oxycelluloses is to some extent an accidental measurement determined not only by the extent of oxidation but also by the amount of alkaline ash constituents."

These authors found that oxycelluloses which had undergone a similar washing treatment to the one herein described, but with sulphuric instead of hydrochloric acid, had in general much higher ash alkalinities than those given in the table, the ash alkalinity being proportional to oxygen consumption, so long as the latter did not exceed about 40 milliatoms per 100 gms. of material. They found that Methylene Blue absorption also, measured under specified conditions, was proportional to oxygen consumption over the same range. For more highly oxidised samples, however, this proportionality no longer held.

The " —COOH values" referred to in the present paper have been found, on the other hand, to be approximately proportional to oxygen consumption over a considerably wider range. They do not appear to depend upon alkaline ash content, except in so far as they may possibly be subject on account of it to some correction, which, for the more highly oxidised samples, would be relatively small.

It cannot yet be claimed definitely that these —COOH values represent carboxylic acid content stoichiometrically. It seems reasonable to suppose, however, that they do so at least approximately, and that the relatively simple method described may be more capable of development into a true stoichiometric determination than that of Methylene Blue absorption.

Measurements of the p_H of Solutions of Sodium Chloride in Contact with Oxycellulose.

Applying the Donnan principle to the system :

Cellulose Phase. Solution Phase.

(1)	(2)
—COOH	H ⁺
—COO ⁻	Na ⁺
Cl ⁻	Cl ⁻
H ⁺	
Na ⁺	

we obtain the equilibrium relationships

$$\begin{aligned} Na_1 + H_1 &= Cl_1 + \text{—COO}^- \\ Na_2 + H_2 &= Cl_2 \\ H_1/H_2 &= \frac{Na_1}{Na_2} = \frac{Cl_2}{Cl_1} \end{aligned}$$

where H_1 , Na_1 , etc., represent ionic concentrations, which are here assumed to represent ionic activities. To express concentrations in the cellulose phase one may make use of the somewhat arbitrary value 0.22×10^{-3} litres per gram of cotton—for the amount of water associated therewith which was employed by Hanson, Neale and Stringfellow³ in the paper already mentioned.

From the above equations, if the sodium chloride and hydrogen-ion concentrations in the solution are known, one may calculate an ionisation constant for the carboxylic acid groups present in an oxycellulose, the effect of lactone formation being neglected. If the —COOH value found by titration be C milli-equivalents per 100 gms., then, since this represents total acidity, we have :

$$\text{—COO}^- + \text{—COOH} = \frac{C \times 10^{-3}}{0.22} \text{ eqivs./litre,}$$

where —COO⁻ and —COOH represent concentrations.

By equating the total sodium ion content of the system to the total amount of chlorine present we obtain the value of $Na_2 - Cl_1$ in terms of H_2 (which is given by p_H measurement) and other known quantities. It is then easy to evaluate H_1 , —COO⁻ and —COOH, by making use of the Donnan equations, and to calculate an ionisation constant

$$k_A = \frac{H_1 \times \text{—COO}^-}{\text{—COOH}}.$$

Measurements of the p_H of sodium chloride solutions in the presence of oxycelluloses were carried out with a "Cambridge" Glass Electrode Potentiometer. The results, and the calculated values of k_A are shown in Table II. :—

TABLE II.

No.	Oxycellulose.		NaCl Solution.		p_H .	k_A (calc.).
	COOH Value Milliequivalents/ 100 Gms.	Dry Weight Gms.	Molality.	Vol. (c.c.).		
3	3.69	1.00	0.855	25	3.55	0.062×10^{-3}
7	6.32	1.00	0.855	25	3.15	0.210×10^{-3}
5	8.42	1.00	0.855	20	3.00	0.328×10^{-3}
12	20.0	1.00	0.855	25	2.63	1.15×10^{-3}

It will be seen that k_A is not constant, but increases markedly with increasing —COOH value. A possible explanation is that, as oxidation proceeds, a greater proportion of the carboxylic acid groups formed lie in close proximity to one another in the cellulose structure, leading to a mutual enhancement of their degree of ionisation. This might happen

if, for instance, chain rupture occurred in positions adjacent to primary alcoholic side-chains which had already been oxidised, with subsequent oxidation of the newly formed terminal groupings to carboxylic acid groups.

The values found for k_A are of the order of magnitude which might be expected for a hydroxy-carboxylic acid. Compare :

Salicylic acid	$k_A = 1.0 \times 10^{-3}$
2.3 dihydroxy-benzoic acid	$k_A = 1.14 \times 10^{-3}$
Gluconic acid	$k_A = 0.25 \times 10^{-3}$

It may be of interest to compare the values calculated for k_A by the foregoing method with those which would be obtained if the carboxylic acid were regarded as uniformly distributed throughout the whole system and the simple law of mass action applied :

$$k_A = \frac{H^+ \times COO^-}{COOH}.$$

Thus for 1 gram of oxycellulose No. 12, in 25 c.c. of salt solution, we have

$$\begin{aligned} \text{Total concentration of acid} &= \frac{20}{25 \times 100} \text{ equivs./litre} \\ &= 8 \times 10^{-3} \end{aligned}$$

$$H^+ = -COO^- = 2.34 \times 10^{-3} \text{ equivs./litre}$$

$$\text{whence } k_A = \frac{(2.34)^2 \times 10^{-3}}{5.66} = 0.93 \times 10^{-3}.$$

A similar calculation for oxycellulose No. 3 gives :

$$k_A = 0.054 \times 10^{-3}.$$

These are evidently of the same order of magnitude as the "constants" obtained on the basis of a two-phase system, and clearly indicate that the assumption of an arbitrary value for the water absorption has no serious effect on the result.

E. Schmidt's Method of Determining Carboxyl Groups in Cellulose by Conductimetric Titration.

Schmidt and co-workers³ claim to have measured the acidity of un-oxidised cellulose by conductimetric titration. An attempt was made to

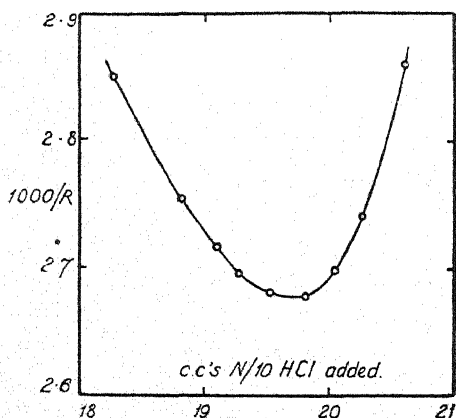


FIG. 2.—Showing variation of conductivity during electrometric titration.

repeat their experiments, using a special type of conductivity cell constructed according to their specifications, and following, in essentials, their experimental procedure. One gram of Tootal's Tarantulle, which had been thoroughly freed from cations by the washing process already described, was cut up very finely and placed in the cell, containing 30 c.c. of N/15 sodium hydroxide solution free from carbonate. 20 c.c. of CO₂-free distilled water were added to wash down cotton particles adhering to the sides of the vessel.

The cell was allowed to stand for about half an hour with a stream of CO₂-free air bubbling

through its contents. This bubbling was continued during the subsequent titration with $N/10$ HCl, and served the further purpose of keeping the mixture well stirred.

A typical conductivity curve obtained by this method is shown in Fig. 2.

In contrast with the schematic diagram given by Schmidt, whose paper includes no experimental curves, this curve shows no points of sharp inflection, and it is impossible to deduce from it where that stage of the titration corresponding to the change $-\text{COO}^- + \text{H}^+ \rightarrow -\text{COOH}$ begins or ends.

Schmidt³ has also carried out titrations of cotton with dilute sodium hydroxide, using thymolphthalein as indicator. As already pointed out, however, methods of direct titration have been found unreliable. In further experiments, in which Schmidt's own technique was followed, the titre showed a continual drift over periods of more than an hour. The final values obtained, moreover, lead to a figure only about one quarter as large as that given by him for the carboxyl content of unoxidised cellulose (0.08, in place of 0.28, gms. CO_2 per 100 gms. cellulose).

Lüttke's Method for Determining Carboxyl Groups.

Lüttke⁵ has described a method in which cellulose is titrated with dilute caustic soda in the presence of a large excess of calcium acetate, using phenolphthalein as indicator. This method also was found to be unsatisfactory, presumably owing to the buffering effect of the acetate. In titrations carried out upon 1 gm. of material, the end-point was quite indefinite over a range of from two to three c.c. of $N/50$ alkali, corresponding with an uncertainty of from four to six milli-equivalents of $-\text{COOH}$ per 100 gms. of cellulose.

Since unmodified cellulose absorbs, or reacts with, the hydroxyl ion in alkaline solutions,¹¹ reliable results using indicators turning at p_H values greater than 7 can hardly be expected.

Summary.

1. A method has been devised for determining the carboxylic acid groups in oxycelluloses.

2. The method has been applied to a number of oxycelluloses, with a view to relating the carboxylic acid value to the conditions and extent of oxidation.

3. The p_H of solutions of sodium chloride in contact with various oxycelluloses has been determined. From the results obtained, making use of the Donnan principle, an attempt has been made to calculate an ionisation constant for the carboxylic acid groups present in oxycellulose.

4. Methods described by Lüttke, and by Schmidt and his co-workers, for determining acid groups in cellulose, have been examined, and found to be unsatisfactory.

¹¹ Neale, *J. Text. Inst.*, 1931, **22**, 320T.

THE COAGULATION OF LATICES BY POLAR-NONPOLAR LIQUIDS.

By F. K. DANIEL, H. FREUNDLICH, AND K. SÖLLNER.

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I.

So many substances have been used as coagulants for latices, particularly for Hevea latex, that it would have been surprising if organic liquids, both soluble and poorly soluble ones, had not been tested. Ethyl alcohol is known as "one of the oldest coagulating media."¹ The amount necessary for coagulating is very large: more than 500 c.c. of ethyl alcohol (96 per cent.) per litre undiluted Hevea latex are needed to bring about complete coagulation (in several hours). Hence we are dealing with a marked change of the medium of dispersion. Occasionally experiments have also been made² with liquids not miscible in all proportions with water and aqueous solutions, such as toluene, chloroform, amyl alcohol, etc. The experimental conditions were, however, often not well defined. Such liquids cause the rubber particles to swell after some time (minutes or hours), and the changes caused by the swelling are not always readily distinguished from those due to mere coagulation.

When experimenting with Abiarana Gutta-percha latex we became interested in organic coagulants.³ This latex is not coagulated irreversibly by electrolytes. The only way so far known to coagulate it, is to add large amounts, e.g., 80 or more parts of ethyl alcohol or acetone to 100 parts of diluted latex. Various organic substances soluble in water, such as methyl, propyl, isopropyl alcohol, ammonium lactate, sodium benzoate, etc., were tested; none was more effective as a coagulant than ethyl alcohol or acetone. On trying, however, a number of organic liquids which are but poorly soluble in water, it seemed that fairly simple and straightforward results might be obtained by using diluted latex, adding so much of the liquid that a second phase is formed and shaking vigorously. With the majority of liquids the stability of the Abiarana latex is not affected; the two phases separate again unchanged after some minutes. Several liquids were found, however, which coagulated the Abiarana latex completely within a few seconds, producing a lump of gutta-percha which floats mostly at the interface aqueous solution/organic liquid.

Comparing the coagulating with the non-coagulating liquids, it became obvious that only liquids which are not miscible with water in all proportions and the molecules of which have a distinctly polar-nonpolar structure are able to coagulate the Abiarana latex in this way. Substances with nonpolar molecules are inactive. By polar-nonpolar structure we mean that the molecules consist of a nonpolar part, such as an alkyl group, and of

¹ O. de Vries, *Estate Rubber*; Batavia, 1920, p. 214.

² H. Lecomte, *Soc. d'Etudes Colon.*, 1902, p. 677, reviewed by C. O. Weber in *India Rubber J.*, 1903, **25**, 19; Vernet, *Caoutchouc et Gutta-percha*, 1920, **17**, 10193; O. de Vries, *Rec. Trav. Chim., Pays-Bas*, 1923, **42**, 701; *Arch. Rubbercultuur*, 1925, **9**, 631.

³ F. K. Daniel, H. Freundlich, and K. Söllner, *Trans. Faraday Soc.*, 1936, **32**, 1570.

a polar part, such as hydroxyl, carboxyl, keto, amino or similar groups, which have a strong affinity to water.

The liquids tested are given in Table I.

TABLE I.

The polar-nonpolar liquids mentioned coagulate the diluted Abiarana latex mostly very rapidly; some like ethyl acetate and ethyl acetoacetate a little more slowly, after some 15 to 20 seconds vigorous shaking.

Diluted Hevea, Funtumia and Jelutong latex are also coagulated in this way by the polar-nonpolar liquids mentioned in Table I., whereas they

Nonpolar Substances
(No Coagulation).

Petroleum ether
Paraffin oil
Dekalin
Carbon tetrachloride
Chloroform
Tetrachloroethane
n-Butyl chloride
Benzene
Toluene
Cyclohexane
Tetralin
Chlorobenzene
 α -Bromonaphthalene
Nitrobenzene

Polar-nonpolar Substances
(Coagulation).

n-Butyl alcohol
Isobutyl alcohol
n-Amyl alcohol
Isoamyl alcohol
Capryl alcohol
Isobutyric acid
Valerianic acid
Methyl formate
Ethyl formate
Methyl acetate
Ethyl acetate
Ethyl malonate
Ethyl acetoacetate
Cyclohexanol

are left unchanged with nonpolar liquids. This does not seem to agree with some earlier results,⁴ probably owing to a difference in the manner of procedure: By shaking vigorously we disperse the organic liquid as rapidly and finely as possible in the latex and allow it to separate as a second phase, when shaking has stopped. During this short process of coagulation the latex particles remain practically unchanged, whereas previous experimenters appear to have left the organic liquid for a long time in touch with the latex, the latter not having been diluted. Then, of course, the swelling of the latex particles (and other processes needing a longer time) may cause changes similar to coagulation in the true sense of the word; in our case coagulation is particularly successful, if the organic liquid separates quickly from the aqueous phase.

II.

The coagulation by organic liquids, observed in our experiments, is probably due to the following mechanism. The latex particles in the latices mentioned are more or less hydrophilic owing to films of proteins or other substances coating them.⁵ They therefore remain in the aqueous phase and are not accumulated at the interface, if the latex is shaken with a nonpolar liquid whose droplets are markedly hydrophobic. If, however, a polar-nonpolar liquid is used, two new factors have to be taken into account:

(a) These liquids are, as a rule, more soluble in water than the nonpolar liquids; hence the dissolved molecules of the organic substance may be adsorbed by the latex particles, thus making them less hydrophilic. These liquids may act like the collectors in the flotation process, which are adsorbed by the particles of the valuable minerals, thus suppressing their tendency to remain in the aqueous phase and favouring the accumulation in the foam,⁶ the latex particles corresponding to these mineral particles. The importance of a certain degree solubility is exemplified by the fact that polar-nonpolar liquids, which are higher

⁴ Cf. 2. The figures given by Lecomte for the coagulation of Landolphia latex by a series of alcohols—from 100 for methyl alcohol to 9 for amyl alcohol—do not disagree with our results. These figures are not coagulation capacities, but the amounts of alcohol necessary to coagulate the same amount of rubber.

⁵ This holds good, for instance, in the case of Abiarana latex, mentioned above.

⁶ Cf. for instance W. Petersen, *Schwimmstoffbereitung*. Dresden and Leipzig, 1936, p. 134, *et seq.*

members of a homologous series, are generally not such good coagulants. Moreover, the tendency of the latex particles to swell quickly is greater with these substances. This first point is presumably the most important.

(b) A second point may also be of influence: The interface latex/polar-nonpolar liquid is less hydrophobic than the one towards a nonpolar liquid. The molecules of the polar-nonpolar liquid are probably oriented in part with their hydrophilic group towards the aqueous phase. Somewhat hydrophilic particles, such as latex particles, may therefore accumulate more easily on the less hydrophobic interface.

In flotation, the mineral particles accumulate in large amount on the surface of a stable foam. In our case the aim is somewhat different, the latex particles being coagulated, and separated from the second phase, the organic liquid. This takes place when the droplets of the organic liquid unite, when shaking stops, the particles being driven together in a layer of the interface which decreases more and more in size during the separation of the two phases. As indicated above, the instability of the emulsion seems to be an important point of this coagulation process. This fits in with the fact that the latex of *Ficus elastica*, stabilised with NH_3 , can also be coagulated by shaking with polar-nonpolar liquids. The process, however, does not work so efficiently as in other cases, because the organic liquid is emulsified in the latex to a fairly stable emulsion. This latex contains a soap-like substance, probably an ammonium salt of a resinic acid, which acts as emulsifier.

III.

The coagulation by some of the lower members of the homologous series deserves brief discussion. In the case of ethyl alcohol or acetone, the amount of coagulant necessary is so large that the nature of the medium is strongly altered. The theoretical conceptions of Kruyt⁷ on the hydration and electrical charge of particles in hydrophilic sols may probably be applied here, the presence of electrolytes being of great importance. A few other cases, however, are interesting.

If 5 to 10 per cent. of iso-propyl alcohol are added to diluted Abiarana latex the gutta-percha may be coagulated partly, provided that the liquid is vigorously shaken. The mechanism of this process appears to be similar to that discussed above: On shaking, an unstable foam is formed which acts like the unstable emulsion formed with a polar-nonpolar liquid. The alcohol adsorbed on the latex particles makes them sufficiently hydrophobic to be accumulated to a certain extent on the surface liquid/air, the air bubbles being surrounded by an orientated layer of organic molecules as are the droplets of the polar-nonpolar liquid. The parallelism to the action of a collector in flotation is still more pronounced than in the cases discussed above. When the foam collapses, the particles are suddenly strongly driven together and thus coagulated. The activity of the air as a second phase is proved by the fact that if the system is moved without producing foam (*as e.g.*, by rolling a test tube filled with Abiarana latex + 10 per cent. iso-propanol (calculated on the diluted latex) quickly to and fro for 15 min.), there is no coagulation. Propanol behaves like *iso*-propanol, but somewhat less strongly.

It is rather surprising on the other hand that butanol and *iso*-butanol behave differently from propanol and *iso*-propanol. The former substances are mentioned in Table I. as coagulants when present as a second liquid

⁷ Cf. H. R. Kruyt, *Colloids*, New York, 1930, p. 197, *et seq.*

phase. If, however, concentrations are taken at which butanol and *iso*-butanol are soluble in the aqueous solution (below 12 and 9 per cent. respectively), the Abiarana latex is not coagulated by these substances. This is the more anomalous, as one would expect the butanol compounds to be better adsorbable on the latex particles than the propane derivatives. The decisive point seems to be that the foam formed by butanol and *iso*-butanol is much more stable than that formed by propanol and *iso*-propanol; a stable foam is distinctly disadvantageous to coagulation, because the latter process only takes place if the bubbles collapse or the droplets of an emulsion are unstable, as explained above.

Phenol, though a polar-nonpolar liquid, is an exception to the rule given in Table I. It does not coagulate Abiarana latex, even if present as a second liquid phase.

There are therefore exceptions to the rule. This is probably in part due to the fact that we have neglected details about the orientation of the polar-nonpolar molecules at the interfaces, a factor of decisive importance; ⁸ unfortunately not enough is known about the actual orientation of the molecules under various circumstances.

It may be open to discussion, whether our explanation, based on the orientation of polar-nonpolar molecules, holds quite generally with different kinds of latices. If the particles are coated with protein (or some other substance), the polar-nonpolar liquid may produce some other change in the surface layer, a denaturation or coagulation of the protein, for instance, which might also favour the accumulation of the particles at the interface of the two liquids.

IV.

Jelutong latex provides an example, of the manner in which coagulation by organic liquids may differ from that by electrolytes and may have special advantages. This latex is more a resin than a rubber system. In the sample we used 19.85 per cent., (*i.e.*, nearly 80 per cent. of the total dry content of the latex) consists of resins or resin-like substances. If Jelutong latex is coagulated by acetic acid, a sediment is formed which is sticky and more plastic than elastic.

If, however, Jelutong latex, stabilised with NH_3 and not having been in contact with air for any length of time, is shaken vigorously with a suitable polar-nonpolar liquid, *e.g.*, *iso*-butanol, amyl or *iso*-amyl alcohol, a lump of rubber is formed at the interface of the two liquids. It has excellent elastic properties and contains only very little foreign matter: it contained 21.5 per cent. of the total dry matter, the percentage of pure hydrocarbon in the latex being 21.2 per cent.

The resins are dissolved or peptised in the organic solvent. When the latter has been separated from the aqueous phase and the liquid distilled off, the resins are found as a perfectly transparent mass (without any yellow component), insoluble in water, hard, dry and not at all sticky at room temperature; 65.1 per cent. of the total dry matter was obtained as resins.

Since Jelutong latex does not behave as an ampholyte and is only coagulated slowly by acetic acid, the coagulation by organic liquids can also be done with an acid latex. The results are not equally good. The coagulation is more rapid, it is true, as is the rule, if the particles are partly discharged. But the coagulum of rubber is less dry and elastic and it contains more foreign substance (23.9 per cent. instead of 21.5 per cent. of the total dry content). The amount of resins found in the organic liquid

⁸ Cf. the behaviour of collectors in flotation (W. Petersen,⁶) and the importance of orientated adsorption for the swelling of starch and collagen in solutions of organic substances (J. R. Katz and collaborators, *Biochem. Z.*, 1933, 263, 421; 1934, 271, 54, and preceding papers). In the latter cases too the influence of phenol upon swelling was found to be the reverse from that of all other polar-nonpolar substances.

was correspondingly smaller, 62.2 per cent. only. Probably resinic acid is formed, on adding acid, from the resin soaps present in the alkaline latex; this resinic acid is less soluble in the aqueous phase than the soaps and is therefore partly precipitated with the rubber.

Summary.

(1) Diluted latices—Abiarana Gutta-percha latex was specially investigated—may be coagulated by shaking them with organic liquids, not miscible with water in all proportions, provided that the liquids form a second liquid phase and that their molecules have a polar-nonpolar structure (butyl alcohol, *iso*-butyric acid, cyclohexanol, etc.). Nonpolar liquids (petroleum ether, chloroform, etc.), do not coagulate diluted latices on shaking under these conditions.

(2) This coagulating action can be explained by assuming that the latex particles are strongly accumulated at the interfaces of polar-nonpolar liquids and water; this is not the case with nonpolar liquids.

(3) Small concentrations of some polar-nonpolar substances of small molecular weight, soluble in water, can also coagulate Abiarana Gutta-percha latex, if they form unstable foams; this was observed with propanol and *iso*-propanol. If the foam formed under these conditions is stable, as with small concentrations of dissolved butanol and *iso*-butanol, no coagulation takes place. This behaviour can be explained as in (2), the air bubbles behaving like the second liquid phase.

(4) Jelutong latex is known to contain an excess of resins, compared with the amount of rubber. A method of coagulating this latex, quickly and separating the resins from the rubber consists in shaking the latex for some seconds with certain polar-nonpolar liquids, forming a second liquid phase, such as *iso*-butyl or *iso*-amyl alcohol. A lump of rubber is accumulated at the interface of the two liquids, the resins are contained in the organic phase.

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THE DIAMAGNETISM OF ORGANIC SULPHUR COMPOUNDS.

BY ARCHIBALD CLOW AND JAMES M. C. THOMPSON.

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The method of calculating diamagnetic susceptibilities formulated by Gray and Cruickshank¹ has proved of such value in investigating structure^{2, 3} that it is desirable to extend it to elements other than those discussed by Gray and Cruickshank, more especially to sulphur, for which the data in the literature are almost non-existent, but which nevertheless gives rise to an important group of organic derivatives. Up to the present the only recorded susceptibilities of organic sulphur compounds are those measured by Pascal,⁴ *viz.* :—

¹ Gray and Cruickshank, *Trans. Faraday Soc.*, 1935, **31**, 1491.

² Clow and Thompson, *Nature*, 1936, **138**, 802.

³ Clow, *Trans. Faraday Soc.*, 1937, **33**, 381.

⁴ Pascal, *Ann. Chim.*, 1910, **19**, 56.

and a few organic derivatives of sulphur oxy-acids. From these Pascal obtained his atomic susceptibility constant for combined sulphur⁵ (-15.0×10^{-6}), and concluded that, unlike oxygen, the susceptibility of sulphur would not vary with its mode of combination. Early in the present work however, as more and more sulphur compounds were investigated, it became apparent that if Pascal's method were to be employed, different susceptibilities depending on the mode of combination would have to be adopted for sulphur.

Dimethyl sulphide .	-44.91×10^{-6}
Diethyl sulphide .	-67.88×10^{-6}
Dipropyl sulphide .	-91.82×10^{-6}
Thioacetic Acid .	-38.40×10^{-6}
Thiophene .	-57.50×10^{-6}

The limitations of Pascal's method have been fully discussed by Gray and Cruickshank in consequence of which it is proposed, not to extend the atomic susceptibility constants for sulphur by Pascal's method but to confine the discussion to an extension of the theoretical bond depressions given by Gray and Cruickshank and to apply them to the investigation of some organic sulphur compounds where there is the possibility of alternative structures.

Calculation of Atomic and Molecular Susceptibilities.

Pauling⁶ derived quantum mechanically atomic susceptibility constants by the equation:—

$$\chi = -1.975 \times 10^{-6} \sum_k \frac{n_x^4}{(Z - S_x)^2} \left[1 - \frac{3l_x(l_x - 1) - 1}{5n_x^2} \right]$$

where n = total quantum number, l = the subsidiary quantum number, and S_x is the screening number on electron k . The factor 1.975 depends on the physical constants (e , m , etc.) given by R. T. Birge, *Physic. Rev. Suppl.*, 1929, 1, 1. For successive stages of ionisation this gives the following atomic susceptibility constants for sulphur.

TABLE I.—IONIC SUSCEPTIBILITY
CONSTANTS ($\times 10^6$).

$S^{-2} - 39.40$	$S^{+1} - 19.50$	$S^{+4} - 7.27$
$S^{-1} - 31.50$	$S^{+2} - 14.46$	$S^{+5} - 4.10$
$S^0 - 25.05$	$S^{+3} - 10.50$	$S^{+6} - 1.38$

On molecule formation there is a deviation between the susceptibility of the ideal molecule and the observed susceptibility which however is systematic and in the direction of a depression of diamagnetism, caused actually by a real lowering of diamagnetism as well as by the development

of high frequency paramagnetism. Only for the H—H bond has this depression been calculated quantum mechanically, but the depression for any given bond, *e.g.*, C—S can be obtained on the assumption that the total depression for any molecule is the sum of the individual bond depressions. Thus from the equation:—

$$\chi_M = \sum \chi_A - \sum \Delta_{xy}$$

where χ_M is the experimental molecular susceptibility, $\sum \chi_A$ the sum of the Pauling atomic susceptibility constants, and $\sum \Delta_{xy}$ the sum of the bond depressions, a series of bond depressions Δ_{S-H} , Δ_{S-C} , Δ_{S-S} , $\Delta_{S=C}$, etc.

⁵ Stoner, *Magnetism and Matter*, 1934, p. 470.

⁶ Pauling, *Proc. Roy. Soc., A*, 1927, 114, 181.

will be obtained and applied to the investigation of structure of sulphur compounds.

The Pauling atomic susceptibility constants are for free ions of inert gas structure, which are but seldom realised in nature, and to get over this difficulty the residual charge derived from dipole moment measurements is used and regarded as that fraction of time which the atom under consideration has the neighbouring whole number charge (*vide* Gray and Cruickshank).

TABLE II.

Link.	Moment.	Dist. d .	ΔE .	$\frac{\Delta E}{e} = F$.
$^+H-S^-$	0.8	1.43	0.6	0.13
C-S	1.2	1.83	0.7	0.15
C=S	3.0	1.59	1.9	0.40
C \equiv S	6.0	1.48	4.06	0.85

Table II. gives these residual charges due to unequal sharing of electrons for a number of bonds involving a sulphur atom calculated by the equation:—

$$\Delta E = \mu/d$$

where μ is the dipole moment and d the inter-atomic distance.

Thus to calculate the molecular susceptibility constant a fraction of Pauling atomic susceptibility constant for each atom is taken, the fraction being determined by the above residual charges F , and from this sum the sum of the bond depressions $\sum \Delta_{xy}$ is subtracted.

Experimental.

The diamagnetic susceptibilities were measured with the modified Curie-Chéneveau magnetic balance which has already been described.¹⁰ Constancy of susceptibility was taken as the final criterion of purity especially as a number of the substances investigated are somewhat unstable and are usually obtained in a very impure form. All susceptibilities are relative to pure water = -0.72×10^{-6} , and were measured at 18° C. Throughout the discussion the susceptibilities have been multiplied by -10^{-6} .

In those cases where the substance to be examined was a gas under normal conditions of temperature and pressure the Curie-Chéneveau method was further modified as follows. The gas to be examined was prepared by an appropriate method and after purification was collected in the liquid air trap *a* (Fig. 1) and further purified by fractionation into *b* or *c*. A

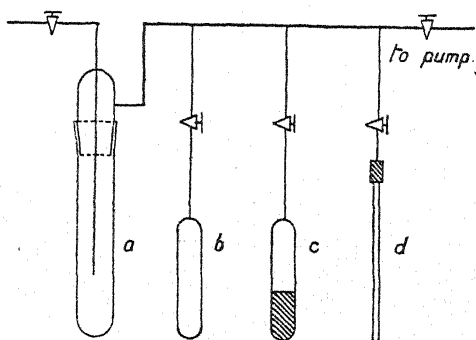


FIG. 1.

glass tube of low susceptibility and suitable dimensions was rounded off at one end and the deflection produced by it in the magnetic balance measured in the usual way, this tube being substituted for the graduated container of the balance. It was then filled with the standard liquid, pure water, and a second deflection obtained. The tube was drawn down in the blow-pipe preparatory to filling, attached at *d* and pumped out, after which it was filled with the required substance by the combined use of

carbon dioxide snow and liquid air by means of which an accurate filling to the required amount could be obtained. While still cooled the tube was sealed off with a small blowpipe flame and a hook attached to it with a small quantity of hard wax. The measurement of the deflection produced by the tube plus liquified gas was then proceeded with as before. Four consecutive measurements of the susceptibility of carbonyl sulphide gave: $+0.537$, $+0.540$, $+0.538$, $+0.540$, *i.e.*, a molecular susceptibility $+32.36 \pm 0.09$, a variation of 0.28 per cent.

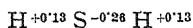
Calculation of Bond Depressions.

(a) **The H—S Bond in Hydrogen Sulphide and Δ_{H-S} .**—The bond depression Δ_{H-S} can be obtained from two sources, the experimental susceptibility of Hydrogen Sulphide $+25.48$ or from the H—S bond in mercaptans, the bond depression Δ_{C-S} having previously been obtained from thio-ethers. The residual charges on the atoms in hydrogen sulphide can be obtained from Table II.,

TABLE III.*—ALL THE KNOWN SUSCEPTIBILITIES OF ORGANIC THIO-COMPOUNDS ARE COLLECTED TOGETHER IN THIS TABLE. ($\times - 10^{+6}$).

Rhombic sulphur .	125.5 I.C.T.
Hydrogen sulphide .	25.48 A.
Carbonyl sulphide .	32.36 A.
Carbon disulphide .	42.29 A.
Ethyl thio-alcohol .	46.97 A.
Propyl thio-alcohol .	58.51 A.
Methyl thio-ether .	44.91 P.
Ethyl thio-ether .	67.88 P.
Propyl thio-ether .	91.82 P.
Phenyl thio-ether .	119.23 A.
Diethyl disulphide .	83.63 A.
Dipropyl disulphide .	106.23 A.
Diphenyl disulphide .	122.49 A.
Thioacetic acid .	38.00 A.
Thioglycollic acid .	49.96 A.
Thioacetamide .	42.45 A.
Thioacetanilide .	89.95 A.
Thiobenzanilide .	123.00 A.
Thiophenol .	71.10 A.
Thiophene .	57.50 P.
Thiobenzophenone .	122.49 A.
Tetramethyl thiourea .	83.93 A.
Tetra ethyl thiourea .	132.60 A.
Tetraphenyl thiourea .	229.74 A.

* I.C.T., International Critical Tables ;
P., Pascal ; A., Authors.



$H^{+0.13}$ implying that the hydrogen atom has the charge H^{+1} for 13 per cent. of the time and H^0 for the rest. So for the whole molecule :—

Number of Atoms.	Time in Different States.	Corros. Pauling Atom. Constants.	Resultant Susceptibility.
2H	13 per cent. in H^{+1}	$H^{+1} = 0$	$0 = 0$
	87 " " H^0	$H^0 = 2.373$	$2(0.87 \times 2.373) = 4.13$
1S	26 " " S^{-1}	$S^{-1} = 31.44$	$0.26 \times 31.44 = 8.17$
	74 " " S^0	$S^0 = 25.05$	$0.74 \times 25.05 = 18.54$
			Total . . . $+ 30.84$

Thus the sum of the atomic susceptibility constants for H_2S is $+30.84$ while the experimental susceptibility is $+25.48$, a difference of $+5.36$ which represents $2 \times \Delta_{H-S}$, giving for $\Delta_{H-S} + 2.68$.

(b) **The C—S Bond in Thio-ethers and Thio-alcohols.**—Three thio-ethers were measured by Pascal ⁴ and these together with diphenyl thio-ether which was measured by the authors are given in the following table. Column three gives the sum of the Pauling susceptibility constants, and column four the bond depressions obtained from them. The depression derived from ethyl and propyl thio-ethers gives for $\Delta_{C-S} + 6.47$.

Thio-ether.	Experimental Suscept.	Σ Pauling Suscept. Consts.	$2\Delta_{C-S}$	4_{C-S}
$(CH_3)_2S$. .	+ 44.91	+ 57.21	+ 12.30	+ 6.15
$(C_2H_5)_2S$. .	+ 67.88	+ 80.93	+ 13.05	+ 6.53
$(C_3H_7)_2S$. .	+ 91.82	+ 104.65	+ 12.82	+ 6.41
$(C_6H_5)_2S$. .	+ 119.23	+ 133.25	+ 14.02	+ 7.01

Using this depression the bond depression in the H—S bond can be determined from thio-alcohols and compared with Δ_{H-S} derived from hydrogen sulphide. To do this two thio-alcohols have been measured: C_2H_5SH + 67.88, C_3H_7SH + 91.82. These alcohols give for Δ_{H-S} + 2.65 which is in excellent agreement with Δ_{H-S} derived directly from hydrogen sulphide, *vis.* + 2.68. The value + 2.65 will be taken as the value of the bond depression Δ_{H-S} .

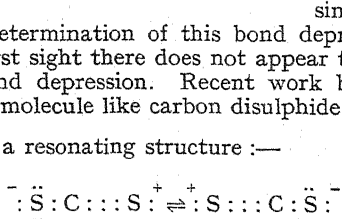
(c) **Alkyl Disulphides and Δ_{S-S} .**—The bond depression for an —S—S—bond was obtained from ethyl and propyl disulphides whose experimental susceptibilities together with the bond depressions derived from them are given in table opposite.

Disulphide.	Experimental Susceptibility.	Δ_{S-S}
$(C_2H_5S)_2$	+ 83.63	+ 9.52
$(C_3H_7S)_2$	+ 106.23	+ 10.64
		Average + 10.08

This value will be further discussed under Applications.

(d) **The Depression in C=S Bonds.**—While simple thio-ketones are unsuitable for the determination of this bond depression on account of polymerisation, at first sight there does not appear to be any difficulty in determining this bond depression. Recent work by Pauling however⁷ suggests that even a molecule like carbon disulphide is not represented by

$:\ddot{S}::C::\ddot{S}: \text{ but by a resonating structure :—}$



and there is also doubt about thio-acetic acid and the thio-amides. With this in view it was decided to take the bond depression $\Delta_{C=S}$ from tetra-substituted thio-ureas about whose structure there can be no doubt (*cf.* Clow, *Trans. Faraday Soc.*, 1937, 33, 381), and from thio-benzophenone. Four bond depressions are given in table opposite.

The somewhat smaller precision of these four bond depressions is readily traceable in thio-benzophenone to its unstable nature, and in tetraphenyl-thiourea to the fact that this is a very large molecule from which to obtain a depression by difference. The average bond depression will be taken as + 20.28, which is the average of all four results or of the middle two, *i.e.*, $\Delta_{C=S}$ is + 20.28.

	Exp. Suscept.	$\Delta_{C=S}$
Thio-benzophenone .	+ 122.49	+ 15.96
Tetramethyl-thiourea .	+ 83.93	+ 20.88
Tetraethyl-thiourea .	+ 132.60	+ 19.65
Tetraphenyl-thiourea .	+ 229.74	+ 24.65

from which to obtain a depression by difference. The average bond depression will be taken as + 20.28, which is the average of all four results or of the middle two, *i.e.*, $\Delta_{C=S}$ is + 20.28.

⁷ Pauling, *Proc. Nat. Acad. Science*, 1932, 18, 293.

(e) Δ_{x-y} for Partially Ionic Bonds.—By methods analogous to those employed by Gray and Cruickshank, the following depressions for partially ionic bonds were determined: $\Delta_{C \rightarrow S} + 1.29$, $\Delta_{C=S} + 2.35$.

TABLE IV.—BOND DEPRESSIONS FOR SULPHUR BONDS.

H—S	+ 2.65
C—S	+ 6.47
C→S	+ 1.29
S—S	+ 10.08
C=S	+ 20.28
C≡S	+ 2.35

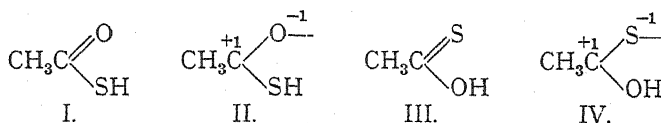
Discussion.

The first essentials are to check the foregoing atomic susceptibility constants and the bond depressions for sulphur by calculating the molecular susceptibility constants of some thio-compounds of known structure and comparing them with the experimental susceptibilities of these compounds. This has been done in the first instance for thio-glycollic acid,

	Susceptibility <i>calc.</i>	<i>expt.</i>
HS . CH ₂ COOH	+ 50.85	+ 49.96

an agreement which is reasonable if not complete.

When the sulphur atom forms part of the $\begin{array}{c} \text{S} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OH} \end{array}$ or $\begin{array}{c} \text{SH} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array}$ group new problems arise on account of resonance as there are now four possible states, *e.g.*, in thio-acetic acid.



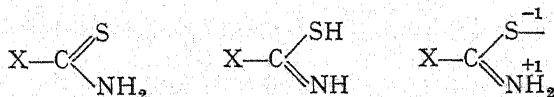
Acetic acid itself resonates between I. and II. The individual molecular susceptibility constants for the above molecules are: I. + 38.75, II. + 48.60, III. + 36.08, IV. + 57.87, while the experimental susceptibility of thio-acetic acid is + 38.00. This indicates that thio-

acetic acid is $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C} \\ \diagdown \\ \text{SH} \end{array}$ without any resonance in the C=O group.

A compound with the sulphur atom attached to a benzene ring has been measured, thio-phenol, susceptibility + 71.10. If one uses the bond depression $\Delta_{C-S} + 7.01$ obtained from diphenyl sulphide, the calculated molecular susceptibility constant for thio-phenol is + 71.68 indicating that there may be a slight difference in the Δ_{C-S} depending on whether it is attached to an aliphatic or an aromatic group.

These results suffice to show that the above atomic susceptibility constants and bond depressions are of such accuracy that one can go on to discuss compounds where there is the possibility of more than one structure arising either from simple tautomerism or resonance.

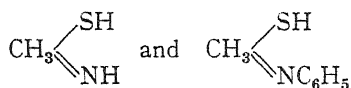
(a) **Thio-amides.**—In thio-amides there is the possibility of three structures:—



each of which will have a different diamagnetic susceptibility. The following table gives the susceptibilities and molecular susceptibility constants of three thio-amides:—

Thio-amide.	Exper. Suscept.	I.	II.	III.
Thio-acetamide .	+ 42.45	+ 40.29	+ 41.56	+ 61.84
Thio-acetanilide .	+ 89.95	+ 81.62	+ 90.82	+ 111.01
Thio-benzanilide .	+ 123.0	+ 118.9	+ 128.2	+ 148.3

These results indicate that thioacetamide and thioacetanilide are represented by



respectively while the deviation in thiobenzanilide may be connected with the development of colour in this compound, an exception to the rule that the simpler thio-compounds are usually white or faintly coloured. It will be noted that there is no evidence whatsoever of Pauling resonance in these thio-amides which is analogous to thio-acetic acid which has already been discussed.

Several results of interest can be deduced from the susceptibilities of compounds already given for the determination of the bond depressions.

(b) Co-ordination in Hydrogen Sulphide.—It has been shown that it is necessary to assume a co-ordinated system to explain the unusually high diamagnetic susceptibility of water, so, in view of the fact that there is less co-ordination in compounds containing a sulphydryl group than in the corresponding hydroxyl compounds the susceptibility should confirm this. The bond depression $\Delta_{\text{H-S}}$ is the same whether it is deduced from thio-alcohols or from hydrogen sulphide itself, which would not be so if the co-ordination in the latter were comparable with that of water, thus showing the absence of co-ordination in hydrogen sulphide.

(c) Disulphides.—Diamagnetism decides in favour of $\begin{array}{c} \text{H} \\ \diagup \\ \text{O} \rightarrow \text{O} \\ \diagdown \\ \text{H} \end{array}$

for the structure of hydrogen peroxide. While H_2S_2 has been isolated its susceptibility is not available but the bond depression for the bond between the two sulphur atoms in alkyl disulphides is known ($\Delta_{\text{SS}} + 10.08$). The order of this result is that expected for an—S—S—

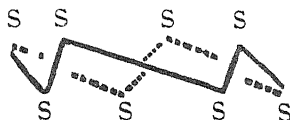
bond and not for the persulphide bond $\begin{array}{c} \diagup \\ \text{S} \rightarrow \text{S} \\ \diagdown \end{array}$, indicating that di-

sulphides are represented by $\text{X}-\text{S}-\text{S}-\text{X}$ and not by $\begin{array}{c} \text{X} \\ \diagup \\ \text{S} \rightarrow \text{S} \\ \diagdown \\ \text{X} \end{array}$ as is to

be expected from their mode of formation.

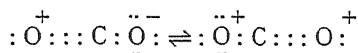
(d) The Diamagnetism of Elemental Sulphur.—Warren and Burwell⁸ have shown that rhombic sulphur is a puckered octagonal ring

⁸ Warren and Burwell, *J. Chem. Physics*, 1935, 3, 6.



linked by two electron valencies. As a result there will be no residual charge on the sulphur atoms and it is interesting to compare the bond depression Δ_{S-S} derived from elemental sulphur with that obtained from organic disulphides. The molecular susceptibility of rhombic sulphur (S_8) is $+125.5$ and the Pauling susceptibility constant for the same molecule $8 \times S^0 = 8 \times +25.05 = +200.4$. The difference between the Pauling molecular susceptibility constant and the experimental susceptibility, $+74.90$, represents the bond depression produced by eight $-S-S-$ bonds; *i.e.*, $8\Delta_{S-S} = +74.90$ or $\Delta_{S-S} = +9.36$. This is a close approximation to $\Delta_{S-S} + 10.08$ obtained from organic disulphides. The agreement between results derived from so different sources is an excellent demonstration of the soundness of this method of dealing with diamagnetic susceptibilities.

(e) Resonance in Carbon Dioxide, Carbonyl Sulphide, and Carbon Disulphide.—From thermal data Pauling and Sherman⁹ deduced resonant structures for carbon dioxide, carbonyl sulphide, and carbon disulphide, of the type:



The diamagnetic susceptibilities of the above compounds are:—

$$CO_2 + 20.80,^{11} COS + 32.36, CS_2 + 42.29$$

and these experimental susceptibilities can be compared with the theoretically possible states of the molecules as given in the following table:—

The large effect of resonance on diamagnetism is brought out in these com-

TABLE V.

	Susceptibility of		Experimental Susceptibility.
	$X=C=X.$	$:\ddot{X}:\ddot{C}::\ddot{X}^+:$	
CO_2	$+ 2.73$	$+ 20.80$	$+ 20.80$
COS	$+ 12.31$	$\left\{ \begin{array}{l} + 38.00 \\ + 42.79 \end{array} \right\}$	$+ 32.36$
CS_2	$+ 22.54$	$+ 59.84$	$+ 42.29$

pounds. In $:\ddot{O}::C::\ddot{O}:$ the residual charges on the atoms are: $O^{-0.42} C^{+0.84} O^{-0.42}$ giving 23.29 for the sum of the atomic susceptibility constants, from which the bond depressions $2\Delta_{C-O}$ have to be subtracted, giving for the molecular susceptibility constant of carbon dioxide 2.73.

If however carbon dioxide is represented by $:\ddot{O}^-::C^+::\ddot{O}^+$ the residual charges become $O^{-1.13} C^{+1.105} O^{-0.025}$ giving 23.22 for the sum of the atomic susceptibility constants. The two bonds are now different, one, $C \rightarrow O$, having a bond depression $\Delta_{C \rightarrow O} = 0.42$, the other, $C \Leftarrow O$, a

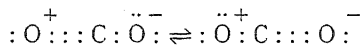
⁹ Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606.

¹⁰ Gray, Clow and Cruickshank, *J. Scient. Inst.*, 1936, **13**, 13.

¹¹ Stoner, *Magnetism and Matter*, 1934, p. 274.

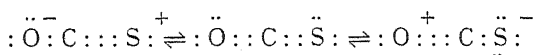
bond depression $\Delta_{C\leftarrow O} = 2.0$ which together have to be subtracted from the sum of the atomic susceptibility constants. Thus the molecular susceptibility constant of $:\ddot{O}^{\ominus}:C::O^{\oplus}:$ is 20.80. The constants for the thio-derivatives are calculated similarly, using the bond depressions for partially ionic bonds given in Table IV.

Neither of the calculated values for the structures $O=C=O$, $O=C=S$, $S=C=S$, agrees with the experimental susceptibility, as is to be expected, but in the case of carbon dioxide a resonance:—



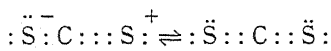
would give a susceptibility of + 20.80 which is exactly what is found experimentally.

In carbonyl sulphide two ionic states with slightly different diamagnetic susceptibilities are possible, but direct resonance between these states gives too high a calculated susceptibility constant. The existence of an intermediate $O=C=S$ state however enables the experimental susceptibility to be accounted for.



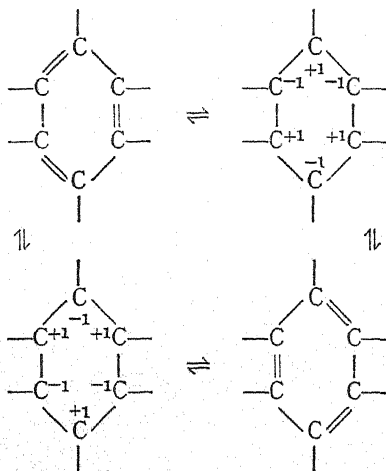
If equal times are spent in these three states the molecular susceptibility constant is + 31.02 compared with an experimental susceptibility of + 32.36.

According to Pauling there is a fall in resonance energy in passing to carbon disulphide and in agreement with this a resonance between



is suggested by the diamagnetic susceptibility of carbon disulphide whose experimental susceptibility is + 42.29 compared with a molecular susceptibility constant of + 41.19 for the above resonating system.

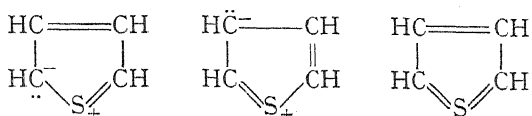
(f) Benzene and Thiophene.—In order to account for the diamagnetic susceptibility of benzene it is necessary to assume that benzene is represented by a resonating system of two Kekulé and two internally ionic states,



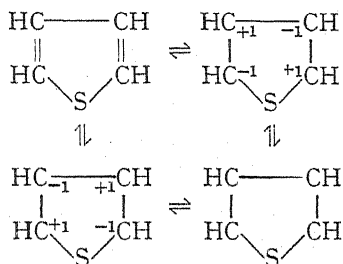
for which the molecular susceptibility constants are + 36.95 and + 73.12 respectively, the average of which, + 55.03, is in complete agreement with the experimental susceptibility. The similarity in the physical properties of benzene and thiophene is already well known and also holds for their diamagnetic susceptibilities.

	<i>Benzene</i>	<i>Thiophene.</i>
Experimental suscept.	+ 55.03	+ 57.50
Mol. suscept. const. for Kekulé structure	+ 36.94	+ 39.57
Difference	+ 18.09	+ 17.93

It was this large difference (+ 18.09) between the experimental susceptibility and the molecular susceptibility constant for a Kekulé structure that necessitated the internally ionic state in benzene and the almost identical difference just given (+ 17.93) indicates that a similar system may be necessary for thiophene. Pauling⁹ has suggested



as possible resonant structures for thiophene but the molecular susceptibility constants of these states are not in agreement with the experimental susceptibility. It is possible, however, that thiophene is represented by a system more akin to that for benzene



This system involves two bonds $\text{C}^{+1}-\text{S}$, $\text{C}^{-1}-\text{S}$ for which it is not possible to give definite bond depressions although by analogy they are probably small. Neglecting these bond depressions the double bonded state and the internally ionic state have + 39.57 and + 74.98 respectively for their molecular susceptibility constants, the average of which + 57.78, as in benzene, is close to the experimental susceptibility, + 57.50. The full significance of these internally ionic states in benzene and thiophene is not yet apparent but the solution of one will undoubtedly be the solution of the other.

Summary.

The method of calculating diamagnetic susceptibilities given by Gray and Cruickshank¹ has been extended to sulphur compounds, the necessary atomic susceptibility constants and bond depressions for all the usual bonds, $\Delta_{\text{H-S}}$, $\Delta_{\text{C-S}}$, $\Delta_{\text{C-S}}$, etc., being calculated. The susceptibilities of some twenty representative thio-compounds are given, and problems

bearing on the structure of the following compounds are discussed : thio-acetic acid, thio-amides, co-ordination in hydrogen sulphide, disulphides, rhombic sulphur, thiophene, resonance in carbonyl sulphide and carbon disulphide, etc. A modification which enables the Curie-Chéneveau Magnetic Balance to be used for the measurement of the diamagnetic susceptibilities of liquefied gases is described.

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REVIEWS OF BOOKS.

Recent Advances in Physical Chemistry. 3rd Edition and **Recent Advances in General Chemistry.** 1st Edition. By S. GLASSTONE. (London: J. and A. Churchill Ltd., 1936. Pp. vii and 430. Price 15s; Pp. viii and 477. Price 15s respectively.)

Dr. Glasstone's book on *Recent Advances in Physical Chemistry* has now appeared in its third edition. That a revised form of this book should have been called for almost annually since its first appearance, is the most convincing proof of its usefulness. There can be very few students of physical chemistry in this country who have not at one time or another consulted Glasstone's compilation as an introduction to subjects which are not dealt with in the standard works. For the sake of those who have not seen the book, the following titles of the chapters will give an idea of its scope: The Electronic Theory of Valency; The Parachor; Dipole Moments; Molecular Spectra; Homogeneous Gas Reactions; Photo-chemical Reactions; The Properties of Surfaces; Heterogeneous Catalysis; Strong Electrolytes.

Recent advances are at present so numerous that Dr. Glasstone has brought out what is virtually a Vol. II., although it is called *Recent Advances in General Chemistry*. The chapters in this work are elementary introductions to the following topics: Atomic Disintegration; Statistical Methods; Ortho- and Para-Hydrogen; Deuterium and its Compounds; Electron Diffraction by Gases and Vapours; Solubility; The Mechanism of Reactions in Solution; Acid-Base and Salt Catalysis; Simple Organic Free Radicals.

There can be no doubt that this companion volume also will perform a useful function in the current dissemination of new ideas in physical chemistry. The fault of both books is one that is natural, if not unavoidable, in works of this kind. It will, moreover, be instantly rectified by consultation with more detailed treatises upon which the books are admittedly based.

Dr. Glasstone is to be warmly congratulated on his sustained service to the popularisation of physical chemistry.

E. A. M. H.

Elektronentheorie der Metalle. By H. FRÖHLICH. (Leipzig: Julius Springer, 1936. Pp. vii and 386. Price R.M. 27 and R.M. 28.80.)

During the last decade, the theory of metals has developed rapidly, and has now reached a stage at which the foundations of the theory may be regarded as firmly established. This theory now forms a framework within which the physical and structural properties of individual metals and alloys seem likely to find, as many have already found, their explanation in terms of their atomic constitution. The present time is, therefore, eminently suitable for the presentation of a general account of this theory, particularly in a form especially interesting to the experimental physicist. Dr. Fröhlich has now given just such an account.

In the first chapter the fundamentals originally given by Sommerfeld and Bloch, are adequately described. Various well-known special effects are dealt with in the second chapter, for example, electron emission by hot wires, photoelectric effects, and optical properties of metals, etc. The theories of these effects are discussed; the underlying principles being made clear, without overburdening the text with detailed calculations, but with an adequate list of references. Conductivity problems are treated in a straightforward way, though these are possibly the least amenable to simplified treatment. The theory of semi-conductors, their electrical conductivity and optical properties are fully dealt with in a special chapter. An account of the theory of ferromagnetism is given which includes (in an appendix) recent theoretical work on the properties of the transition metals and their alloys. A chapter is also devoted to the important problem of metallic binding treated according to the theory of Wigner and Seitz. An introduction to this chapter, based on a "free electron model" seems to the reviewer of doubtful value.

The book contains 38 tables, mainly giving comparison between theory and experiment, and 71 well-designed diagrams.

H. J.

Annual Reports on the Progress of Chemistry, 1936. Vol. XXXII. (London, The Chemical Society. Pp. 512. Price, 10s. 6d., postage 6d.)

This valuable report is again to be welcomed. Almost one half of it is of direct interest to readers of these *Transactions*; nearly 100 pages are devoted to General and Physical Chemistry and 32 pages to Crystallography. Many other interesting reports, for instance, in the sections on inorganic, and on organic chemistry, relate to matters on which papers have appeared in these pages or recall meetings of the Faraday Society and help us to visualise subsequent progress. Apart from these, however, there is given to us an excellent opportunity of seeing in a small compass the advances made in the fields less known to us.

Of the reports devoted more particularly to subjects in which this Society interests itself, particular mention may be made of those by Glasstone on "Electron Diffraction and the Structures of Gaseous Molecules" and on the "Effect of the Solvent in the Measurement of Dipole Moments," by Adam on "Surface Chemistry and Colloids," and by Moelwyn-Hughes on "Chemical Kinetics."

These reports are clearly written and if the reviewer has on occasion to admit lack of understanding he willingly, though sadly, accepts his own ignorance as the explanation, rather than any obscurity on the part of the reporter. Those who fail with him will be in a minority. When he comes, however, to the report on the "Quantum Mechanics of Molecules" he still does not blame the reporter, but he is no longer in a minority. Indeed so vast are the numbers of those to whom quantum mechanics is a sealed book, which indeed might as well be written in Urdú, that very few can be expected to understand it. It is very doubtful whether the report is worth while. Apart from those experimentalists whose facts are, or are not, in accord with the reported quantum mechanical calculations, there appear to be about two dozen workers in the field. Doubtless these few and a handful of others will appreciate the real value of the report, but one is tempted to ask whether the same end could not have been met by circulating a typewritten copy. Indeed, most readers (unless like the reviewer they insist on trying to subjugate an incipient inferiority complex) will read the first sentence: "Although quantum mechanics defines quite clearly a mathematical process by which the energy of formation of a molecule from atoms may be calculated, computational difficulties have prevented much progress from being made in all but the simplest cases." And, having read, will sigh regretfully, or with relief, according to temperament, and skip the next seventeen pages.

A Complete Physics (written for London medical students). By W. H. WHITE. (London: Richard Clay & Sons., 1936. Pp. vii and 848, Price 15s.)

Mr. White's book is *different*. It is a thoroughly competent and scholarly volume, admirably suited to the needs (and wants) of elementary students—that is, of students of the intermediate grade. Nothing essential is omitted, and the student can be assured that, whether he desires a competent knowledge of elementary physics, or whether his immediate object is to pass an examination, Mr. White will lead the way, a trustworthy guide who will beguile the journey

"With learning put lightly, like powder in jam."

Mr. White writes well and lightheartedly, and his scholarship is as sound as his writing. Tested on those small points, such as, for example, the interpretation of Newton's law of cooling, points on which the average textbook writer is apt to be either vague or wrong, Mr. White shows that he realises the advisability of going to original sources.

And his lightest asides have a purpose. Even the most case-hardened examiner will thank him for the pregnant sentence with which he opens his treatment of the eye—

"There are two c's and two m's in accommodation."

The book is well produced and illustrated, and has very full sets of questions, numerical examples, and practical problems appended to each section.

A. F.

Tungsten: A Treatise on its Metallurgy, Properties and Applications. By COLIN J. SMITHELLS. 2nd Edition. (London: Chapman & Hall, Ltd., 1936. Pp. 272. 183 illustrations, including photomicrographs. Price 25s. net.)

The first edition of this book was published ten years ago, and since that time many developments in the metallurgy of tungsten have taken place, so that the revision has been considerable. It may seem strange that the physical constants of tungsten, until recently one of the rarer metals, should be known with greater accuracy than those of almost any other metal. The reason is that its principal applications lie in the field of electrical technology, the development of which is not only recent, but has been throughout in scientific hands. For the successful use of tungsten at high temperatures it has been necessary, in the first place to prepare the metal in a state of high purity, and in the second to determine its physical properties with a high degree of accuracy. The preparation of the metal on a commercial scale follows the lines of a laboratory process, and the special technique (reduction of the oxide in a powder form, followed by electrical sintering in hydrogen and swaging) has served as a model for the production of other difficultly reducible metals.

Tungsten offers many points of interest to the metallurgist and physicist, such as the effects of added substances on crystal growth, and the still unexplained discontinuities in the physical properties at very high temperatures. Tungsten was the first metal to be studied intensively in the form of single crystals, and its high melting-point and great cohesion make it a very suitable material for studies of deformation at different temperatures. Some of the photographs are of great interest, especially the beautiful structures of crystals exposed by vacuum etching (Fig. 52).

The importance of tungsten is not confined to the metal, and separate chapters are contributed to this edition by experts, J. H. G. Monypenny having written on tungsten steels, and T. R. Bird on tungsten carbide and its uses, the most important of which is for hard cutting tools, made by uniting the carbide particles to a compact mass by sintering with a metal, usually cobalt. These alloys have brought about a revolution in the drawing of wires and in the rapid machining of many alloys. A chapter of physical interest, by A. L. Reimann, deals with the thermionic properties of tungsten, the metal being used both in the bare and in the coated form as an emitter. An account of observations of thoriated tungsten at different stages of activation, made with the electron microscope, is included.

The book may be fully recommended as a thorough monograph on a subject of great technical, and also of scientific importance.

C. H. D.

Hand- und Jahrbuch der Chemischen Physik. Bd. 8. Abschn. II. Lichtzerstreuung. By H. A. STUART and H. G. TRIESCHMANN. (Akademische Verlagsgesellschaft M.B.H. Leipzig, 1937. Pp. x and 191, with 76 illustrations. Also index for Sections II. and III. Price M. 24.)

This book is in two sections, the first by Stuart on scattering in the region of the visible spectrum, and the second by Trieschmann on scattering

of Röntgen rays by atoms and molecules. Together they form an exhaustive survey of one branch of the important field—the interaction of light and matter.

The investigation of the scattering of light from small particles has been very helpful in many branches of physical chemistry. In colloidal chemistry, it has led to a more exact knowledge of the size, shape and concentration of the particles in colloidal solutions and the Raleigh scattering from molecules has proved to be of importance in yielding information about the structure of liquids and molecular anisotropy. The scattering of light from fluctuating groups of molecules, which under special circumstances appears as a critical opalescence, gives us an insight into the mode of grouping of molecules in liquids and crystalline liquids and the most recent development in this field, the Raman effect, has had a very direct bearing on the theories of molecular structure. H. A. Stuart deals very clearly and concisely with all of these phenomena, giving the detailed mathematical basis of the outstanding classical and wave mechanical theories, and outlines of the practical methods of measurement. A valuable list of data is given of the degree of depolarisation for chemical substances, and these data are important for the light they throw on molecular anisotropy. The section on the Raman effect treats with this phenomenon mainly from the theoretical aspect, the reader being referred to other monographs including that of Teller in volume IX. of the same series for further information.

The section by Trieschmann deals with the scattering of Röntgen rays from the free electron, from the electron shells of atoms and from molecules in the gaseous, liquid and solid states. Frequent comparisons are made between the experimental scattering curves and those derived theoretically, but in the case of solids and liquids this is as yet only possible in a few simple cases. The author summarises the experimental technique and compares the utilities of the Röntgen ray and electron beam methods. The importance of the Röntgen ray scattering for chemistry lies mainly in the knowledge it provides with regard to interatomic distances and these are summarised as far as known and the values are compared with those obtained from the Raman effect, infra red spectra, etc. Its importance for settling doubtful points of structure is emphasised, and special reference is made to cis-trans isomerism. A four-place table by H. Sherman of $\sin \pi/\lambda$ is included.

W. E. G.

A Comprehensive Treatise on Inorganic and Theoretical Chemistry.

By J. W. MELLOR, D.Sc., F.R.S. Longmans, Green & Co., London, 1936. Pp. viii + 816. Price, 63s. net.

In this volume 497 pages are devoted to Nickel, 47 to Ruthenium, 47 to Rhodium, 94 to Palladium, 44 to Osmium and 59 to Iridium. The volume thus deals with a group of elements which have served for some of the most interesting modern investigations in the field of inorganic chemistry, as exemplified by the work done at Birmingham, Cambridge, and Teddington. Apart from Nickel, these elements are also of increasing technical importance. There are many examples of delightful phrasing as on page

592: "The individuality of allopladium has been admitted by faith without the presentation of an accredited passport." But the volume seems definitely inferior to the previous ones. It lacks much, not only in clarity, but also in that accuracy which is so essential for a work of reference.

C. H. S.

Catalytic Reactions at High Pressures and Temperatures. By V. N. IPATIEFF. (London, Macmillan, 1936. Pp. xxii + 786. Price 30s.)

This book is described by the author as his chemical autobiography, and consists largely of a collection of original publications on catalytic reactions. These are classified into separate chapters dealing with dehydrogenation, dehydration of alcohols, decomposition of acids, isomerisation, hydrogenation, condensation, polymerisation and alkylation.

The descriptive matter will chiefly appeal to organic chemists, as it makes easily accessible a vast amount of preparative detail which has often previously appeared only in Russian journals, or in highly condensed form in books such as Ellis's *Hydrogenation of Organic Substances*. The results obtained by the high-pressure treatment of complex ring systems, for example, are of particular interest to those engaged on the investigation of heterocyclic compounds. As a historical record of pioneering work the book will also be valued, especially in connection with the development of high pressure technique, but it is unfortunate that so much material of a polemical character has been introduced. The work of the past few years, carried out in America, is described in the concluding chapters which contain a good deal of hitherto unpublished material. A large proportion of this is concerned with polymerisation or alkylation under the influence of acids or halogen compounds, similar to those employed in the Friedel-Crafts reaction. In an appendix, the application of such processes to the petroleum industry is recorded, and it is clear that further developments in this direction should prove of much practical importance.

Theoretical treatment of the subject is dispersed throughout several sections, although two separate chapters are devoted to the question of promoter action and to general theoretical principles. Particular attention is paid to the action of mixed catalysts, to the state of oxidation of the catalyst surface, and to the function of water in catalytic reactions. The author's difficulties in this discussion are considerably increased by the autobiographical method adopted, and by limitation to organic reactions. Although the views expressed are often at variance with the opinions of other workers, and do not take into consideration the full evidence available, it is of interest to have a clear record of the ideas of one who has devoted so many years to practical investigation of the subject.

The amount of experimental data included in the book is unusually large, and might be somewhat abbreviated without affecting its utility. Reference to the tables and drawings would be facilitated by more frequent titles and headings, but the index has been very competently compiled, and the translation into English is uniformly good.

R. H. G.

Die Fermente und ihre Wirkungen. Supplements 2 (1935) 3, 4, 5 and 6 (1936) by Prof. CARL OPPENHEIMER. (Junk: The Hague, Holland.)

These volumes are part of a supplement to the special part of the 5th edition of Oppenheimer's textbook, published in 1924-29.

The present numbers are 2 of a series of 10, and bring up-to-date Sections VIII. and IX. of Volume I.

Applied Chemistry for Engineers. By A. F. H. WARD. (London: Longmans Green. Pp. xi and 127. Price 5s. net.)

This little book contains an interesting collection of experiments on such matters as are related to the engineer's problems: water analysis, boiler water treatment, corrosion coal and oil. It is intended, in some 100 hours, to complete by specialisation the chemical equipment of the engineering student who has finished a first year's course. If the student can be persuaded to take an interest in this work he will, when practising as an engineer, more nearly approach to an understanding of the meaning and value of the work of his chemist colleague.

Instrument Transformers. By B. HAGUE. (London: Isaac Pitman & Sons, 1936. Pp. xxiv, 656, and 21. Price 35s.)

One has to deal with figures of astronomical magnitude when one attempts to compute the value of the electrical energy developed in a year in the world's generating stations and transmitted to consumers by, in general, polyphase alternating currents. Obviously the accurate measurement of this energy is a matter of the first importance. Equally obviously, with the growth in magnitude of the currents and voltages generated, came the necessity, as a matter of safety and convenience, for connecting the measuring instruments to the supply network, through suitable transformers. Hence the appearance of the instrument transformer.

Readers of Dr. Hague's treatise on Alternating Current Bridge Methods will look forward to a full and scholarly treatment of this topic, and they will not be disappointed. It is impossible to review in any detail the contents of a volume which presents an attempt at a complete analysis of the very extensive literature which has accumulated round the subject of the instrument transformer. It is sufficient to say that the book is divided into five sections, which deal respectively with the theory and characteristics of instrument transformers, the apparatus used in testing instrument transformers for ratio and phase-angle, the testing of current transformers for ratio and phase-angle, the testing of voltage transformers for ratio and phase angle, and additional tests on both types of transformer. Despite the large mass of detail handled, there is a unity of treatment and outlook which makes the book very pleasant reading. It is a notable contribution to the literature of electrical engineering.

A. F.

THE PROPERTIES AND FUNCTIONS OF MEMBRANES, NATURAL AND ARTIFICIAL.

A GENERAL DISCUSSION.

Thursday, 22nd and Friday, 23 April, 1937.

THE SIXTY-SIXTH GENERAL DISCUSSION of the FARADAY SOCIETY (being the Fifth Colloid Meeting organised by the Colloid Committee of the Faraday Society, which comprises representatives of the Royal Society, the Biochemical Society, the Chemical Society, the Faraday Society, the Physical Society, the Physiological Society, and the Society of Chemical Industry) was held in the Chemistry Theatre of University College, London, on Thursday and Friday, 22nd and 23rd April, 1937.

The subject was considered under the following heads:—

Part I. Natural Cell Membranes: (a) *General:* (Structure, Permeability, Membrane Potential, Anaesthesia. (b) *Special:* (i) Red Cells; (ii) Fish Gills, Egg Membranes, etc.; (iii) Plant Cells; (iv) Bioelectric Phenomena: Nerve, Muscle, Skin; (c) *Narcosis.*

Part II. Artificial Membranes.

At the inaugural meeting the President (Professor M. W. Travers) welcomed the overseas guests and members, who were received with acclamation; those so welcomed were: Professor L. R. Blinks (*Stanford*), Professor R. Collander (*Helsingfors*), Mrs. M. M. Brooks (*Berkeley, California*), Professor and Mrs. Gorter (*Leiden*), Dr. P. Grabar (*Paris*), Professor H. Handovsky (*Ghent*), Professor Ancel Keys (*Rochester, Minn.*), Frl. Dr. D. Kruger (*Berlin*), Dr. Maaskant (*Leiden*), Professor E. Manegold (*Dresden*), Professor H. Mark (*Vienna*), Dr. M. Mathieu (*Paris*), Professor and Mrs. Kurt H. Meyer (*Genthod Geneve*), Dr. J. van Ormondt (*Leiden*), Professor W. Ostwald (*Leipzig*), Dr. F. Schutz (*Vienna*), Dr. and Mrs. H. de Witt Smith (*New York*), Professor S. Tchakhotine (*Paris*), Dr. T. Teorell (*Uppsala*), and Dr. W. Wilbrandt (*Bern*). At the request of the President the Chair was then taken in succession by Professor R. A. Peters and by Professor E. K. Rideal.

By the courtesy of the Provost the Guest Night Dinner was held at University College on Friday, 23rd April.

At the conclusion of the meeting, votes of thanks were accorded to the authors of papers, the Provost of University College and to Professor Donnan and his staff, to the organising committee, and to Professor Tchakhotine for his exhibition of apparatus and experiments.

The Report of the Meeting, including all the papers contributed, together with the discussion thereon, appears in the following pages.

PART I.—NATURAL MEMBRANES.

INTRODUCTORY PAPER: ANIMAL MEMBRANES.

BY AUGUST KROGH.

Received 22nd March, 1937.

There is, I believe, some ambiguity regarding the proper use of the word membrane in animal physiology and I feel it necessary therefore to define the sense in which I shall use the term. I take a membrane to be a structure (with main extension in two dimensions only) which will restrict the free movement of molecules or particles, but will not by expenditure of energy bring about any transport of substances across its thickness. To my mind this distinction, though often disregarded, is absolutely essential. Membrane function, as here defined, is the function of a definite *fixed structure* (for the time being) which can, in favourable cases, be studied by relatively simple means. Active transport of a substance is brought about by some kind of *dynamic machinery* working within living cells, which may in their turn be bounded by membranes allowing certain substances to pass through and holding others back. I maintain that such membranes are, in the present state of our knowledge, definitely unsuitable for the study of membrane properties, because it is too difficult to distinguish the membrane from the cell of which it is an integral and perhaps variable part. I hope to make clear what I mean in some of the examples which follow.

I shall begin by attempting some sort of crude classification.

1. Surface "Membranes" of Cells.—As a rule these are ill-defined, probably highly variable in structure and properties in one and the same cell and so closely bound up with the "protoplasm" of which they form the boundary zone that they cannot even be clearly recognised as membranes. I contend that these are on the whole ill-suited for the study of membranes, although there are certain very conspicuous exceptions. The red cell membrane of the mammal is an almost ideal object of study, being morphologically distinct, and also because we have every reason to believe that no energy exchange takes place within the cell-body. The study of the "vitelline" membrane of eggs of several species may yield significant and useful information, when the energy transformations undoubtedly taking place within the eggs have no definite relation to the membrane.

2. Exudation Membranes—Non-living structures produced in the first instance by exudation from living cells and thereupon more or less modified by hardening, imbibition with other substances, oxidation, etc. The "chitin" membranes of insect epidermis and tracheæ and the "chorion" membranes of many animal eggs are cases in point. I submit that these membranes, being in some cases fairly simple and more or less similar to artificial membranes, should receive much more attention than has been the case so far.

3. Membranes made up of cells or syncytia having, so far as we know, membrane functions only, being unable to provide any active transport.

Dealing with this group caution is necessary, because it is difficult to be certain that no active transport is taking place.

The cells making up such membranes are thin with very flat nuclei or (sometimes) without visible nuclei, in which case it seems fairly certain that true membrane functions only can be exercised. The glomerular syncytial epithelium of vertebrates is a good example, the vascular endothelium is another. The placental membrane is generally assumed to be of this type and nothing is known to me which could exclude it. The urinary bladder of several kinds of vertebrates and the swimming bladder of fishes present cellular membranes which should be accessible to a quantitative study. The pulmonary epithelium of higher vertebrates and the branchial of fishes and many lower animals would also generally be referred to this type, but many cells are present which do not conform to specifications, and in some cases these are known to perform work in the transport of substances.

4. Finally we have a large number of complicated structures which may, and often do, function as membranes in certain respects, but which have at the same time definite transport functions and are therefore on the whole ill adapted to the study of true membrane functions. A clear-cut example is the epithelium of the kidney tubules the different sections of which have definitely different active transport functions (for water, sugar, etc.). The intestinal epithelium is often treated and discussed as a membrane, although there is an active transport of several substances which interferes seriously with the membrane properties. Again a large number of experiments have been made on frogs' skin treating it as a "simple" membrane and describing "differential permeability" and so on, while actually we have the membrane properties complicated and obscured by active transport processes.

Before discussing briefly a number of examples I want to emphasise the functional point of view. The function of membranes is often largely mechanical. The exoskeleton of Arthropods, the "chorion" membranes of many types of eggs and the epidermis of animals generally are cases in point. We are, however, more interested in the physico-chemical function which is generally protective against the passage of certain substances, so that membranes can be defined by a more or less selective permeability. Very remarkable combinations of permeabilities seem to be possible in the animal kingdom, but there are certain limits which bring about a conflict of interests and a consequent compromise. It would be of value for example to many aquatic animals to have their external surface impermeable to water, but such impermeability seems to be incompatible with a sufficient permeability to oxygen.

In discussing by way of examples a small number of animal membranes referred to the classification given above I leave out purposely the cases of red cells and of Echinoderm eggs which have been most extensively studied, but with which I am personally only superficially acquainted.

1. The eggs of freshwater animals, when laid, generally possess an osmotic pressure presumably the same as that of the parent organism, and it is an interesting problem how they can keep up sufficient inorganic salts for development and avoid swelling. In the case of trout eggs,¹ an initial swelling takes place by osmotic water uptake, but after three to six hours the vitelline membrane becomes impermeable not only to salts, but to

¹ (a) Gray, *J. exp. Biol.*, 1932, 9, 277. (b) Irving and Manery, *J. Cell. Comp. Physiol.*, 1934, 5, 457. (c) Krogh and Ussing, *J. exp. Biol.*, 1937, 14, 35.

water, and this state is maintained until the time when, presumably, the embryo's kidneys begin to function. During this period the metabolism is low, but O_2 and CO_2 do pass through the water impermeable vitelline membrane at the measured rate of 4 mm.³ per cm.²/hour. The outer "chorion" membrane has mechanically protective qualities, but seems to be freely permeable to all relevant substances.

Some other fish eggs are known to show an initial swelling, but quantitative measurements, for which the eggs are eminently suitable, do not seem to have been made so far. The eggs of marine teleosts also present corresponding osmotic problems, only in their case the surrounding medium possesses the higher concentration.

2. The properties of the insect exoskeleton have been studied in a number of cases by Wigglesworth,² and several older notions have been profoundly modified. What was called the chitinous cuticle of insects is generally composed of two layers, a very thin epicuticle which is soluble in boiling potassium hydroxide and an endocuticle composed of chitin and an insoluble protein. Before an insect moults the new cuticle is formed inside the old by the epidermal cells while new tracheæ are laid down surrounding the old. Between the two layers a fluid is present in which Wigglesworth failed to detect chloride, but could obtain colour reactions for protein. This fluid dissolves the endocuticle which is reabsorbed, but leaves the epicuticle intact. The freshly formed cuticle must therefore be freely permeable to water and to dissolved substances of large molecular size, and when at any time it is chloride free it must be the cellular epidermis which is either impermeable or actively absorbs the ions, a power which is very widely distributed in the animal kingdom.

At moulting the whole of the fluid is generally absorbed. A similar absorption takes place from the tracheal system. Shortly afterwards the new soft cuticle hardens by oxidation or by imbibition with some substance from within, or more probably by both processes, and it becomes as a rule impermeable to water, slightly permeable to oxygen, while it is apparently always somewhat permeable to CO_2 . There are, however, considerable differences between different cuticles.

I have measured³ the permeability to oxygen and nitrogen of the cuticle from the body wall of an *Oryctes* larva 0.054 mm. thick and found figures which are about 1/10 of those for mammalian connective tissue or 3.8 per cent. of those for water.

The cuticle of the tracheal gills of many aquatic forms (*Odonata*) is permeable to water (and, of course, to gases), and as a rule the cuticle of gills is permeable to certain organic substances like urethane.⁴ In many forms, like the chironomids, the general body surface is freely permeable to water while certain regions are permeable to ions. It appears therefore that cuticles can be produced showing all grades of permeability like collo-dion membranes, but conditions are complicated by the presence of the epicuticle. However, the mainly epicuticular skins of insects as left by the moulting process will in some cases be well suited to permeability experiments.

The cellular membranes in the body show a wide range of differential permeability. Their properties are closely bound up with their vitality and are often profoundly but reversibly influenced by narcotics, poisons or oxygen lack. The cellular membranes proper are very thin, but they are often, like the epithelium of the swimming bladder in fishes, the urinary bladder and the endothelium of blood vessels above capillary size, supported on substantial structures containing connective tissue and smooth muscle. The swimming bladder and the urinary bladder show a high degree of impermeability. The swimming bladder is, according to Bohr,⁵ almost im-

² Wigglesworth, *Insect Physiology*, London, 1934.

³ Krogh, *J. Physiol.*, 1919, **52**, 391.

⁴ Krogh, *Internat. Revue Hydrobiol.*, 1914, **6**, 42.

⁵ Bohr, *J. Physiol.*, 1893, **15**, 494.

permeable to gases as shown by the oxygen pressure remaining constant at above 50 per cent. for more than twenty-four hours in the bladder removed from the fish.

For the urine bladder of man Rehberg⁶ has given me the following figures. By 1 mole concentration difference about 0.06 millimole of Cl and 0.03 of urea will diffuse out per cm.² per hour. These organs probably merit a closer study, and I shall discuss as examples membranes of which a little more is known.

3. The vascular endothelium is generally permeable to gases, water and crystalloids, but more or less impermeable to colloids. In frogs a filtration of fluid containing about 1 per cent. protein is taking place in the skin capillaries all the time, causing the whole of the plasma to leave the vessels and return through the lymph system about once an hour,⁷ but in mammals the lymph circulation is much slower, and it is a controverted question whether the filtrate from capillaries contains about 1 per cent. protein⁸ or, as I hold, 0.1 per cent. or less.

Mechanical stretching of the capillary wall brought about by relaxation of the contractile elements causes a pronounced increase in permeability,⁹ allowing, when pushed beyond a certain point, all the plasma to escape and producing *stasis* by filling the distended capillaries with closely-packed corpuscles. In many tissues this is a reaction to noxious stimuli, and it is doubtful whether the individual capillary will recover, but Knisely¹⁰ has shown by his beautiful observations that in several organs, and notably in the spleen and in the liver, we have a definite mechanism utilising this change in permeability. Certain capillary vessels designated as sinusoids will at regular or irregular intervals become closed by a kind of sphincter at their venous end. They will swell, filter off all the plasma through the dilated walls and finally become completely packed with corpuscles which they may retain for a considerable period and discharge by opening the venous sphincter. Single red corpuscles often slip out through the walls of these sinusoids, but always without leaving any opening.

Landis¹¹ measured by a very ingenious micro-method the normal filtration rate of capillaries in the frog's mesentery and arrived at a figure which can be expressed as 0.034 ml./cm.²/minute/atm. and which can be increased to about 0.09 before the capillary wall becomes definitely permeable to protein, and he found further that in these vessels poisons like alcohol in 10 per cent. concentration would increase the permeability by changing the wall without affecting the diameter of capillaries. Lack of oxygen would also increase the permeability, while CO₂ or other acids within p_H values between 8.0 and 6.0 have no influence. When oxygen was re-admitted within a few minutes the change in permeability was perfectly reversible, and the very important fact is demonstrated that a normal metabolism is a necessary condition for these cells to maintain their normal permeability.

It is an important result of Landis' experiments that the same rate of fluid movement through the normal capillary wall was brought about by the same pressure whether this acted from inside out as an excess filtration pressure or from outside in as an excess osmotic pressure. In both cases we do not have any diffusion of ions or particles, but the fluid moves in bulk, and all solutes which are able to pass through the wall are carried along without any separation. This will still hold even for particles of comparatively very large size. In experiments to determine the absolute permeability of the capillary wall by means of semi-colloidal and colloidal

⁶ Rehberg, *Bioch. J.*, 1926, 20, 447, 461.

⁷ Churchill, Nakazawa, and Drinker, *J. Physiol.*, 1927, 63, 304.

⁸ Drinker and Field, *Lymphatics, lymph and tissue fluid*, Baltimore, 1933.

⁹ Krogh, *Anatomie und Physiologie der Kapillaren*, Berlin, 1929.

¹⁰ Knisely, *Anat. Rec.*, 1936, 65, 23.

¹¹ Landis, *Amer. J. Physiol.*, 1928, 81, 124; 82, 217; 83, 528.

stains it was shown by Landis that such substances as vital red and trypan blue, which are able to pass the capillary wall, diffuse so slowly that their passage cannot be detected, while they are carried out rapidly by a sufficient filtration pressure. The electric charge of the particles did not seem to make any difference.

The membrane characteristics of the capillary wall can only be studied by micro-manipulative methods and even with these any high degree of accuracy can scarcely be attained. It must be admitted, moreover, that the conditions defining these characteristics are difficult to establish and that the properties of the endothelium probably vary greatly from one tissue to another. It is significant that histamine, which so strongly affects mammalian capillaries and small vessels generally, is indifferent to the blood vessels of the frog.

4. The syncytial epithelium of the kidney glomeruli is much better defined, and on man fairly accurate estimates of filtration rate and absolute permeability can be made. Vimtrup¹² counted the glomeruli in the human kidney and estimated the total glomerular surface at 15,000 cm.². The intra-glomerular pressure causes filtration of a fluid which, as shown by Richards¹³ for the frog's kidney, contains all the crystalloids of the plasma in the exact proportion in which they are found in a blood ultrafiltrate, demonstrating again that we have to do with a transport of fluid in bulk. Rehberg⁶ measured the rate of filtration in the human kidney by introducing creatinine up to a suitable concentration in the plasma and comparing the concentration of creatinine in the plasma with the corresponding concentration and quantity in the urine, making the assumption that all the creatinine appearing in the urine was filtered off in the glomeruli and that nothing diffuses back during the passage through the tubuli. This assumption has been doubted, and other substances have given somewhat different figures for the filtration, but Rehberg's result has been amply confirmed for the dog and the rabbit and can be taken as substantially correct. The most recent and convincing confirmation was obtained by Richards¹³ using inulin, a substance possessing according to Westfall and Landis¹⁴ a molecular weight of 5100 and being very unlikely to diffuse back into the blood.

According to Rehberg⁶ the maximum filtration in the human kidney, produced when all glomeruli are functioning, is 200 ml. per minute. The filtration pressure is difficult to estimate, but is generally taken to be about 0.1 atm. and this would give a filtration of 0.13 ml./cm.²/minute/atm. or about 50 per cent. higher than that observed by Landis¹¹ in capillaries just impermeable to protein.

The absolute permeability of the glomerular membrane is defined by the molecular weight (5100) of inulin which passes through and the molecular weight of the smallest protein molecules (68,000) which are quantitatively retained.

In pathological cases of nephrosis the glomeruli become permeable to the smallest protein molecules, and lack of oxygen definitely increases the permeability.¹⁵

5. The pulmonary epithelium separating the lung capillaries from the air in the alveoli shows some similarity to ordinary endothelium and is taken as permeable to water and crystalloids, but in the meshes between the capillary loops cells are present which may very well perform active transport work, and it appears difficult to explain the absorption of edema fluid from the alveoli as anything but active transport. In the normal lung no edema is produced and this is probably a simple function of the colloid osmotic pressure of the blood.

¹² Vimtrup, *Amer. J. Anat.*, 1928, 41, 123.

¹³ Richards, *Harvey Lectures*, New York, 1935.

¹⁴ Westfall and Landis, *J. Biol. Chem.*, 1936, 116, 727.

¹⁵ (a) Starr, *Amer. J. Physiol.*, 1925, 72, 184. (b) Grande Covian and Rehberg, *Skand. Arch. Physiol.*, 1936, 75, 21.

Gases pass through by simple diffusion, the direction and rate of passage always clearly depending upon the pressure gradient. The permeability to CO_2 being high the arterial blood leaving the lungs is always practically in equilibrium with the alveolar CO_2 pressure. The oxygen pressure in the arterial blood as taken from arteries is regularly found to be definitely lower (some 15-20 mm. Hg) than in the alveolar air, and an attempt has been made by Sarre¹⁶ to deduce from this difference a diffusion constant for oxygen through the capillary wall and including, of course, the diffusion in the plasma and corpuscles and the combination of oxygen with hemoglobin. The figure obtained by such a calculation is very low and would involve a very large pressure difference during muscular work and at low oxygen pressures. Actually the pressure difference observed during muscular work is unaltered or slightly increased, while at low oxygen pressures it is much reduced, and it becomes necessary therefore to postulate profound changes in the conditions for diffusion. The whole argument is unconvincing, because the arterial blood as measured has had an admixture, probably small, but quantitatively unknown, from venous blood through the bronchial blood-vessels and perhaps another through the Thebesian veins in the heart, an admixture which is probably responsible for most of the tension deficit observed at normal pressure during rest.

An essentially different way of determining the diffusion rate from the alveolar air to the blood is to measure the rate at which CO is taken up from a known low CO percentage in the alveolar air.¹⁷ In these determinations it is assumed that the CO pressure in the blood remains so low as to be practically negligible, and a personal constant is calculated representing the volume (in ml.) of CO which will diffuse in (and become combined) per minute per mm. pressure difference. This figure is individually variable (between 18 and 35 ml.). For the same person it depends upon the volume of air in the lungs, being above a certain mean volume proportional to the $4/3$ power of the air volume and below that volume independent of volume changes. This is explained by the assumption (for which there is histological evidence) that below the critical volume the epithelium becomes folded while the surface remains constant, while above that volume the epithelium is stretched and its thickness reduced accordingly. Because the constant includes the passage of the gas within the blood and the combination with hemoglobin it is not independent of the blood flow, but increases somewhat with the increased flow during work, e.g. from 32 to 42 when the circulation rate is increased from four l./minute to twenty-four l./minute.

The constants as found and recalculated for oxygen (an increase of 23 per cent.) are just about quantitatively sufficient to explain the oxygen intake during the heaviest type of muscular work or at very low oxygen pressures, but the work of Hartridge and Roughton¹⁸, showing that the combination of CO with hemoglobin is a definitely slower process than the corresponding combination with O_2 , has made the assumption untenable that the CO pressure in the blood during diffusion determinations is practically 0, and the diffusion constants for oxygen must therefore be higher by an unknown amount.

6. The branchial epithelium of fishes. While the actual pulmonary surfaces cannot be measured with such accuracy as to make calculations of absolute permeabilities worth while, branchial surfaces and thicknesses can be measured and have been measured in a small number of forms, but the measurements have not so far been seriously utilised. For individuals of the same species the branchial surface is found to be proportional to the general body surface or to the $2/3$ power of the weight,

¹⁶ Sarre, *Z. Biol.*, 1934, 96, 352.

¹⁷ (a) Krogh, *M., J. Physiol.*, 1915, 49, 273. (b) Bøje, *Arb. physiol.*, 1933, 7, 157.

¹⁸ Hartridge and Roughton, *Proc. Roy. Soc., B*, 1923, 94, 336.

and for different species reduced to 1 g. weight the surfaces given by Pütter¹⁹ work out as varying between 2 and 9 sq. cm., rather small figures when the external body surface is about 10 cm.² for 1 g. I measured on a trout of 190 g. a body surface of 346 cm.² or for a 1 g. trout $\frac{346}{\sqrt[3]{190^2}} = 10.5$ cm.². The result of Riess²⁰ for a 650 g. pike giving the branchial surface as between 810 and 925 cm.², corresponding to 10.8-12.3 cm.² for a 1 g. pike is, I think, more likely to be representative of fishes in general, but new and careful measurements are evidently necessary.

The branchial membranes generally are, of course, permeable to oxygen and carbon dioxide, but the permeability to water is fairly low and the permeability to ions in many cases doubtful. They seem to be practically impermeable to sugar, but easily permeable to urea and urethane except in elasmobranchs. The gills of freshwater invertebrates (Crustaceans and Molluscs) show permeabilities of the same order, but I have noted⁴ the curious fact that the gills of *Astacus* are practically impermeable to urethane.

In seawater teleosts and in a very large number of freshwater animals (fishes and invertebrates) special cells are present in the gills which are able actively to transfer Cl⁻ ions. In the marine teleosts this transfer takes place from the blood to the outside fluid when the Cl concentration in the blood rises above a certain level.²¹ In the freshwater forms the corresponding cells are able to take up Cl ions from extremely dilute solutions and will do so when the Cl concentration in the blood falls below a certain level. It is an interesting fact that in the eel, where the active transport from the blood to the water was first demonstrated, a transport in the opposite direction apparently cannot take place.

7. The kidney tubules have a cellular lining which it would be a mistake to characterise as a membrane. A diffusion of alcohol takes place to such an extent that a significant concentration difference between the urine and the blood cannot become established, and there is also some diffusion back of urea and other substances,⁶ but different cells function as active transporters of water, glucose (other sugars to a slight extent) and certain ions. The investigations of Richards and co-workers¹³ especially have shown that separate parts of the tubule are responsible for the transport of single substances. A mechanism has been made out which will "explain" the transport of sugars and which may represent in a crude fashion what is actually happening.²²

The cells contain an enzyme which will bring about phosphorylation of glucose and another which will dephosphorylise. If we postulate that glucose can diffuse in through the tubular surface of the cells in question, that it is there phosphorylated so as to keep up a glucose gradient, that it is transported as glucose-phosphate to the surface in contact with the blood and that it is there split into glucose and phosphate allowing the glucose to diffuse into the blood, we have a machine which, supplied with the necessary energy, can be conceived as doing the work.

So far as I am aware this mechanism is the only one suggested for the active transport of a substance, and the task of suggesting corresponding mechanisms for the transport of Cl ions, of oxygen in the gas gland of the swimming bladder, and of water, is no doubt formidable, but it cannot be even approached until it is recognised that we have to do with something which is essentially different from what is taking place in membranes.

¹⁹ Pütter, *Die Ernährung der Wassertiere*, Jena, 1909.

²⁰ Riess, *Arch. f. Naturgesch.*, 1881, 47, I, 518.

²¹ (a) Keys, *Z. vergl. Physiol.*, 1931, 15, 352, 362. (b) Schlieper, *Z. vergl. Physiol.*, 1933, 18, 682; 19, 68.

²² (a) Wilbrandt und Laszt, *Biochem. Z.*, 1933, 259, 398. (b) Lundsgaard, *Biochem. Z.*, 1933, 264, 209, 221; *Shand. Arch. Physiol.*, 1935, 72, 265. (c) Kalcker, *Enzymologia*, 1937, 2.

8. The skin of frogs has been the object of a great deal of experimentation, undertaken on the assumption that it acts as a membrane, and what is termed "differential permeability" for water and ions has been described. Experiments with heavy water ²³ both *in vivo* and on excised pieces of skin failed to show any difference in the rate of D₂O diffusion in the two directions, but comparisons of the diffusion rate with the rate of osmotic exchange of water confirmed Jacobs ²⁴ in showing that osmosis is a fundamentally different process which in the frog's skin is several times more rapid for a given concentration difference than diffusion. Experiments by Huf ²⁵ and others, purporting to show that water travels faster by osmosis from outside in than in the opposite direction, are complicated by the fact that there is a vigorous active transport of Cl ions from the outside in, tending to create a surplus osmotic pressure on the inside. According to Huf's experiments this transport goes on in the isolated skin bathed with Ringer on both sides, while I have found ²⁶ that in the living frog it is a regulated process coming into action only when the salt content of the body is lowered. I have been able to demonstrate the uptake of Cl ions from extremely dilute solutions (less than 10⁻⁴ normal) and further that it is the Cl⁻ ion which is actively transported and can be either accompanied with Na⁺ ions (to a slight extent with K⁺ and perhaps even with a little Ca⁺⁺) or exchanged against the carbonate ion. I mention these facts which in my opinion are not relevant to the subject under discussion, as a warning against the uncritical extension of the membrane conception.

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²³ Hevesy, Hofer, and Krogh, *Skand. Arch. Physiol.*, 1935, **72**, 199.

²⁴ Jacobs, *Ergebn. d. Biologie*, 1935, **12**, 1.

²⁵ Huf, *Pfl. Arch.*, 1936, **237**, 143.

²⁶ Krogh, *Skand. Arch. Physiol.*, 1937, **76**, 60.

GENERAL DISCUSSION.

Professor A. Krogh (Copenhagen) (*communicated*) added: Lundegårdh has recently demonstrated a secretory uptake of anions from very dilute solutions by active cells in plant roots and measures the metabolism necessary to bring about this transport; he further suggests a possible mechanism for this process. The analogy to the active absorption observed in my laboratory in a number of fresh water animals is very striking and I have been able to show for the frogs skin that in addition to Cl⁻ and Br⁻ NO⁻ is also actively absorbed although at a slower rate.

I desire to emphasise again that these active processes, which require energy, should not be classed with membrane properties.

Dr. T. Teorell (*Uppsala*) said:

(1) When discussing "active transport" of a substance by living cell systems as suggested by Professor Krogh, it is advisable to distinguish between *permeability* (ability of penetration) and *driving forces*. The *flow* of the substance across a cell or tissue boundary is proportional to these two independent factors. So far, previous investigators seem to have concentrated on the nature of the permeability (pore-, solubility-theory, etc.). It is generally not at all clear what is meant by driving forces. Hitherto, only the "osmotic" force has been emphasised by biologists, and this has been spoken of as pressure or concentration gradients. If transport of electrically charged particles is considered, another driving force must be taken into account, namely that of an *electrical potential gradient*. This may be located within the boundary or membrane across

which the transport occurs. As can be shown both theoretically and experimentally, the combined influence of osmotic and electrical gradients may lead to transport of material *against* a concentration gradient.¹ Many such "up-hill migrations," in biology described as "active transport," may be related to the existence of a P.D. in the secreting or resorbing area. It should be emphasised that such an effect of a P.D. does not require any actual flow of current (no local current, therefore no identity with electro-phoresis!). Some fundamental problems to be considered in relation to permeability forces are :—(a) The magnitude of P.D. within the cell or tissue boundaries (membranes) performing active transport, (b) The nature of such P.D.'s and how they are maintained.²

(2) The stomach mucosa provides a very suitable object for investigations of permeability problems *in vivo*. The following results were obtained in experiments on narcotised cats.³ The mucosa seemed to show the same behaviour as a collodion sack. Interdiffusion of ions could take place between the stomach contents and the mucosa cells or the blood. Surprisingly, H ions seem to be freely permeable through the mucosa surface. The concentration-time curves were generally pronouncedly exponential, thus allowing an approximate determination of a diffusion constant D . ($C_t = C_0 e^{-\frac{D \cdot A \cdot t}{v}}$, where C_t and C_0 are the conc. at the time t and 0, A is area and v is volume).

The following somewhat averaged figures were found (all solutions were approximately isotonic with the blood) :

A. *Diffusion from the Stomach Cavity into the Mucosa—*

(D figures are given per cm² per minute when the concentration gradient is unity. The figures have to be multiplied by 10⁻³.)

Glucose . . .	0.3	(Na)HCO ₃ . . .	0.6
H(Cl) . . .	1.4	(K)Br . . .	0.7
H(ClO ₄) . . .	2.4	(Na)Ac . . .	0.7
H ₃ (PO ₄) . . .	0.5	(H)Ac . . .	2.5
H(La) . . .	4.3	("free" diffusion	
H(Ac) . . .	7.2	of HCl against	
		water :	
		$D = 1.6 \cdot 10^{-3}$)	

B. *Diffusion of Cl Ions from the Mucosa into the Stomach Cavity—*

Solution in the cavity.	$D \times 10^{-3}$.
H ₂ O	0.2
KNO ₃	0.4
KBr	0.5
HCl	0.7
HLa, HAc	>0.9

The acidity of the weak acids, H-lactic and HAc, is seen to decrease "abnormally" fast, probably because of a solubility effect on the undisassociated molecules.

The possibility of a "back diffusion" to the mucosa of hydrochloric acid initially secreted into the stomach cavity and a simultaneous outward diffusion of alkali chloride from the stomach cells has been suggested as an explanation for the variations of gastric juice acidity (and chloride content).⁴

Professor H. Handovsky (*Ghent*) said: Professor Krogh, in discussing the morphological variations in animal cell membranes, stated that "the membrane is an integral and perhaps variable part of the cell." From a physiological point of view this variability seems to me to be of highest significance and as it does not appear to have been sufficiently emphasised at this meeting, I should like to put forward some suggestions.

Animal cell membranes are, upon one side at least, in contact with colloidal suspensions. If this suspension is blood, the composition is that of sols of different proteins, hydrophilic lipoids, hydrophobic sterols,

¹ *Proc. Nat. Acad. Sci., Wash.*, 1935, 21, 152; *J. Gen. Physiol.*, 1937, *in press*.

² In this connection, see remarks on pp. 1054 and 1086.

³ For details as to the technique see *Skand. Arch. f. Physiol.*, 1933, 66, 225.

⁴ *Loc. cit.*¹ and *Acta Med. Scand.*, 1935, 85, 518.

etc. The numerous studies of single cell (erythrocyte) permeability have shown that many physical properties are altered after the cells have adsorbed colloids upon their surfaces. Other cell membranes, such as those of the blood capillaries, also adsorb colloids. Since the colloid composition of the blood changes under varying physiological and pathological conditions, the cell membrane will then have different exterior layers. These changes may (and occasionally must) considerably alter the behaviour of the cell membrane. Thus, permeability constants, measured by analyses of substances on either side of the membrane, are probably related directed only to the physiological state of the membrane at the moment of measurement, and change with change in the physiological state.

For instance, consider a porous membrane. The laws of diffusion and dialysis, the Donnan equilibrium, determine the permeability of the membrane. If, however, the pores are filled with albumen or with a sterol, the membrane is no longer porous, and other laws, the laws of solubility in the membrane, govern its permeability. As an illustration of the great variability of a membrane under different conditions, I should like to cite one of our experiments: Through an artificial membrane of nitrocellulose (Zsigmondy's *UltrafeinfILTER*), at about one atmosphere pressure, there passed 41 c.cm. of water in 100 minutes. The addition of caffeine (0.3 per cent.) did not affect the velocity of the passage of the water. After a 2½ per cent. serum albumen solution had been passed, however, only 13.2, 13.7, 13.5 c.cm. of water was transmitted in 100 minutes, and none of the albumen went. With a caffeine-serum albumen solution having an albumen concentration of 2½ per cent. and of caffeine 0.3 per cent., the membrane passes 20.7, 21.8, 18.3 c.cm. of water in 100 minutes, and again none of the albumen passes. In this we seem to have a good model for the study of the varying physiological behaviour of a membrane.⁵

Dr. R. B. Dean (*Cambridge*) said: With regard to the mechanism suggested by Professor Krogh for the concentration of glucose by combination with a phosphorus compound in the presence of one enzyme and subsequent breakdown of this compound after diffusion in the presence of another enzyme I desire to call attention to the fact that, so far as I know, enzymes are true catalysts and will catalyse a reaction equally well in either direction. I do not see how the necessary energy could be put into the system.

If there is a flow of a substance such as oxygen across a membrane and this substance forms a complex permeable in the membrane with a substance to which the membrane is impermeable, e.g., a hypothetical $[O_2Cl^-]$ complex, then such a mechanism will supply the necessary energy to transfer a substance against a concentration gradient.

Dr. Ancel Keys (*Rochester, Minn.*) said: The great majority of animal membranes are composed either of living cells or are inseparably associated with living cells. The fact that metabolic processes are taking place in these systems undoubtedly complicates their study, but that is not necessarily a good reason to exclude them from consideration as membranes. Membranes derive their claim to special and separate consideration chiefly because they represent morphological boundaries across which exchanges take place between two phases. From the biological point of view the membrane generally cannot be considered apart from these two phases and, in fact, many membranes such as the surface membranes in cells, can have no separate existence. It must be obvious, then, that of living organisms we usually have to deal with a "system" in which the membrane has a central but not an independent place.

Krogh emphasises the special virtues, for experimental study, of "exudation membranes," because they are themselves inert and are more or less independent of the liquid phases they separate. It will be granted

⁵ See also the former publication of Handovsky and Uhlenbruck, *Klin. Wchn.*, 1925, p. 1401.

that the investigation of the properties and functions of these membranes may be less difficult than in other systems. At the same time it must be admitted that relatively few membranes of biological importance belong to this restricted "ideal" class of structures. From the biologist's viewpoint it would seem to be necessary to be ready to deal with any and all biological membranes, regardless of the fact that most of these membranes may not conform to the simplest first expectations of an ideal, passive equilibrium. Krogh's classification should help much in preventing oversimplifying assumptions; I hope it will not daunt the worker who recognises the difficulties in non-ideal systems from continuing the experimental attack.

Professor E. Manegold (*Dresden*) said: In considering permeation through porous systems it is essential to bear in mind the question whether we are concerned with a capillary system or a space-energy system (*i.e.*, pores of molecular dimensions). If we take a membrane separating reservoirs having concentrations of C_i gm./c.c., on the inlet and C_o gm./c.c., on the outlet sides respectively, the permeability coefficient of a capillary system is defined by

$$\delta^*d = \frac{S}{Ft(c_i - c_o)} \text{ cm.}^2/\text{sec.},$$

where S is the mass, in grams, of matter which at the temperature of the experiment passes in t seconds through F cm.² of a capillary system of thickness d cm.

If, however, we are concerned with a space energy system we take, in place of the difference in concentrations in the reservoirs, the concentration gradient between the inlet and outlet surfaces of the membrane ($c_i' - c_o'$). In the simplest case there is a relationship between the reservoir and the surface concentrations depending on a Henry distribution equation, so that we can write $C_i' - C_o' = \tau(C_i - C_o)$, where τ is the distribution coefficient. For the reduced permeability coefficient (δ^*d), we obtain thus:

$$(\delta^*d)_r = \frac{S}{F \cdot t \cdot \tau(c_i - c_o)} \text{ cm.}^2/\text{sec.}$$

For example, in the case of rubber the two coefficients are, at 25° C.:

$$\begin{array}{ll} \text{CO}_2 (\delta^*d) = 0.99 \times 10^{-6} \text{ cm.}^2/\text{sec.} & (\delta^*d)_r = 1.04 \times 10^{-6} \text{ cm.}^2/\text{sec.} \\ \text{H}_2 & = 0.34 \times 10^{-6} \text{ ,,} & = 34.4 \times 10^{-6} \text{ ,,} \end{array}$$

The order of the two dimensions is inverted in the two cases because τ for CO_2 is about 1 and for H_2 about 0.01. Similar results are obtained for permeation through glass membranes and dried collodion films.

Professor A. Krogh (*Copenhagen*) in reply (*communicated*): Dr. Teorell's suggestion that a potential difference is the driving force in the active transport of charged particles through cells may be correct for some special cases, but more often the selectivity of the transport mechanism is too high to admit this suggested explanation.

The mechanism for breaking down the phosphorus compound of sugar in kidney cells is certainly not simply an enzymatic one, as suggested by Dr. Dean, because the breakdown requires the supply of a considerable amount of oxidation energy, and the same holds for the transport of anions against concentration gradients in plant roots and many animal "membranes."

I agree with Dr. Keys that all biologically important "membranes" should be studied and I am myself engaged upon an extensive study of certain types; I wish, however, to emphasise that they should not be studied as problems in permeability until one is reasonably certain that the "membrane" selected for study is not organised as a highly specialised mechanism for doing transportation work of some kind.

THE CONSTITUTION OF PLANT CELL MEMBRANES.

By W. STILES.

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The problems of the membranes of plant cells, their constitutions and functions, are of considerable complexity and for the most part, in spite of much research extending over many years, unsolved.

In reviewing the present position of our knowledge of the membranes of plant cells it is necessary for us first of all to take note of the general structure of plant cells. Although these vary greatly in size and shape, all plant cells, except young meristematic cells, have the same general structure. Each cell consists essentially of a layer of living substance, the protoplasm, surrounding a central vacuole consisting of a solution of crystalloidal substances such as acids, salts and sugars. The general consensus of opinion to-day is that the protoplasm is a colloidal system, although a variety of views are held regarding the kind of colloidal system, whether suspensoid or emulsoid, or whether essentially a sol or a gel, which constitutes the protoplasm. Surrounding the protoplasm is the cell wall, a membranous structure of varying composition, but in which cellulose is typically the chief constituent. It is clear, then, that in this cell system, there are two obvious structures which can legitimately be regarded as membranes, the cell wall and the protoplasm forming an internal lining to it.

It is, however, usually assumed by botanists that the outermost and innermost layers of the protoplasm differ in constitution from the main mass and so themselves form membranes separating the protoplasm from the cell wall on one side and the vacuole on the other. They are the so-called plasmatic membranes or plasma-membranes. It must be pointed out that these membranes cannot be distinguished under the microscope, so that the evidence for their presence is indirect. It is therefore perhaps not surprising that two diametrically opposed views have been expressed regarding their very existence. "Every protoplast is surrounded by a special dermal layer, the external plasmatic membrane or ectoplast . . . possessed of a special structure, by virtue of which it is able to control many of the relations which the protoplast maintains with the outer world," wrote Haberlandt. Martin H. Fischer, on the other hand, dealing it is true with animal cells, regarded the plasmatic membrane as a figment of the imagination.

It is obvious, however, that for an understanding of the mechanism by which substances enter and leave cells it is necessary to know whether there are such limiting layers to the protoplast acting as membranes, and it is therefore desirable to review the evidence which can now be adduced in support of their presence, and bearing on their nature, if they do indeed exist.

It may here be pointed out that we should be helped towards a solution of this problem if we had tolerably certain information regarding the kind of colloidal system which constitutes the protoplasm. Thus it is a general phenomenon that naked protoplasm brought in contact with water does not mix with it but tends to round up into a sphere. This

may indicate no more than that water and protoplasm are immiscible in the same way that water and oil do not mix, but the more generally held opinion is that the protoplasm is limited by a definite membrane which is largely impermeable to the constituents of the protoplasm and which tends to be regenerated by and from the protoplasm if damaged.

Unfortunately there is far from unanimity of opinion regarding the constitution of protoplasm and the evidence relating to this is contradictory. From measurements of the viscosity of protoplasm, both plant and animal, Heilbrunn concluded that protoplasm must be of the nature of a suspensoid sol, the measured viscosity values being low, at most only a few times that of water. If this conclusion is accepted it forms a strong argument for the existence of a plasma membrane preventing the dissolution of the protoplasm when in contact with water. But other workers, notably Lepeschkin, largely from a consideration of the substances, carbohydrates, proteins and fats, known to be present in protoplasm, conclude that protoplasm is not a simple hydrosol and that the dispersion medium is not water or an aqueous solution but some sort of compound of water, proteins and fatty substances. If this view presents a true picture of the constitution of protoplasm there is no need to hypothesise the presence of limiting membranes to prevent dispersion of protoplasmic constituents into a surrounding aqueous medium.

One line of investigation into the existence of plasma-membranes has been the observation of living cells with the ultra-microscope. There are, however, remarkably few such observations on record, and our information from these is rather fragmentary. But as far as they go they rather favour the view that the limiting layers of the protoplast do differ from the interior. Thus it was observed by Price that in *Spirogyra* smaller particles tend to occur in the outermost and innermost layers of the protoplasm than elsewhere in it, and this layering becomes definitely pronounced when the cells are plasmolysed. In *Spirogyra* there is no indication that these limiting layers are of a gel or solid consistency, for the small particles observed in them display active Brownian movement. On the other hand, in another filamentous alga, *Mougeotia*, where an outer layer differentiated from the rest of the protoplasm is also observable, this layer appears clear with no moving particles, and Price thought that it might be of gel constitution. In the cells of the hairs on the stem and leaves of *Cucurbita*, Price thought he could also make out a fine membrane bordering the protoplasm. On the other hand, no definite differentiation of outer layers could be made out in *Elodea*. But where no membrane could be observed ultra-microscopically, Price thought there was evidence for the existence of a membrane, since the particles in movement do not escape from the protoplasm. But this would presumably be the case if the protoplasm consisted of phases immiscible with the aqueous medium in the vacuole and surrounding medium.

Evidence of about the same degree of definiteness has been derived by the method of experimentation known as micro-dissection or micurgy, in which the effects are observed microscopically of drawing fine glass needles through protoplasm. According to Seifriz evidence is obtained from such observations that the surface layer of protoplasm is much more viscous and elastic than the interior as shown by the greater resistance offered by the surface layer to the movement of the micro-dissection needle. It must, however, be pointed out that grave doubt has been expressed regarding the possibility of estimating with any

degree of accuracy the viscosity of protoplasm by the method of micro-dissection.

A micrurgical experiment which has been held to demonstrate the presence of plasma-membranes consists in the injection of a dye by means of a micro-pipette into the body of the protoplasm. In certain cases the dye diffuses throughout the protoplasm but does not pass out of it. This is held to indicate that the protoplasm is limited by a membrane definitely different in constitution from the rest of the protoplasm, since the dye readily diffuses through the protoplasm but not across its surface. It may, however, be argued against this type of experiment that penetration of the protoplasm by the pipette causes damage and that the observed behaviour is that of abnormal material.

Evidence for the presence of plasmatic membranes has also been sought in the behaviour of plant cells when immersed in water or aqueous solutions. In pure water the cells swell owing to absorption of water and, conversely, when placed in solutions above a certain concentration the cell contents contract away from the wall, exhibiting the condition known as plasmolysis. The cells behave, in fact, just as if they contained a solution, exercising an osmotic pressure, surrounded by a membrane permeable to water and impermeable to the solutes in that solution.

Unfortunately, such observations as far as they concern plant cells have been confined to cells with vacuoles, and the observed results are explained by supposing that the cell wall is completely permeable to water and dissolved substances while the whole protoplasmic layer forms the semi-permeable membrane separating the liquid in the vacuole from that outside the cell. It would be interesting to have similar observations on meristematic cells devoid of vacuoles. They should yield valuable information as to whether the outermost layer of the protoplasm acts as a semi-permeable membrane separating the rest of the protoplasm from a liquid external to the cell.

A great deal of information has been obtained regarding the entrance of dissolved substances into plant cells, but the interpretation of the data, particularly in regard to the possible existence of plasmatic membranes, is rendered difficult on account of the complexity of the system involved. We may follow the entrance of a substance into plant cells by observing the fall in concentration of the substance in the external medium, but such observations in themselves tell us nothing of the fate of the substance in the cell. When a substance is thus observed to enter a cell it may simply accumulate in the cell wall, or it may penetrate the cell wall and accumulate in the protoplasm, or it may pass through the protoplasm as well and enter the vacuole. Recently some Austrian workers have differentiated between "intrability," the passage of solutes into the protoplasm, and "permeability," the passage of solutes through the protoplasm into the vacuole. A number of cases of intrability of dyes have been observed. They can obviously be explained on the view that the protoplasm is bounded by an internal plasmatic membrane impermeable to the dyes in question, but other explanations based on adsorption, solubility and partition coefficients also seem possible.

Similarly, although failure of a substance to enter a cell may be ascribed to impermeability of the outermost layer of the protoplasm, it is equally possible in this case to ascribe it to insolubility of the solute in the protoplasm.

It is of interest to note at this point the great difference observed

in the entrance of electrolytes and non-electrolytes into plant cells. The beautiful work of Collander on the entrance of non-electrolytes into cells of *Chara* indicates that such substances diffuse into the cells just as if they were diffusing through a membrane from one aqueous solution to another, and the position of equilibrium reached appears to be one in which there is equality of concentration on the two sides of the membrane. With electrolytes, on the other hand, this is very far from being the case. Many investigations, including some of my own, have shown that the two ions of an electrolyte may enter a cell at different rates and to different extents, while the process of absorption tends towards a position of equilibrium which is not one of equality inside and outside the cell, but which is dependent on the concentration, the diluter the solution the greater the amount of solute absorbed relative to the concentration. There is much evidence that these processes of absorption are linked with metabolic processes in the cell, but the important point to note here is that an ion can be absorbed by a plant cell so that its concentration is many times higher inside the cell than outside; that is, the entrance of an ion continues against its own concentration gradient. In aquatic plants it has been shown to be generally the case that the concentration of ions in the vacuole is higher than that of the same ions in the external medium.

Such a distribution of ions is suggestive of that in a Donnan equilibrium which results when a membrane separates two solutions of electrolytes one of which contains an ion incapable of diffusing through the membrane. There is every reason to believe that protoplasm may contain such ions; they might, for instance, be provided by proteins. As such an equilibrium requires a membrane separating the two solutions, the observed distribution of ions inside and outside plant cells can therefore be regarded as affording evidence for the presence of a membrane other than the permeable cell wall between the protoplasm and outer solution. But closer inspection of actual data presents a difficulty. Under conditions of Donnan equilibrium the product of the concentrations of the two ions of an electrolyte, as, for example, the potassium and chloride ions of potassium chloride, should be equal on the two sides of the membrane, whereas it is frequently the case in plant cells that the product is considerably greater inside the cell than outside. Of course there are difficulties attaching to the determination of ionic concentrations inside cells, and it is rarely if ever clear how the ions are distributed between the protoplasm and vacuole in the cell. Briggs has suggested that the observed results might be reconciled with conditions of Donnan equilibrium if account is taken of the presence in the cell of the two phases, cytoplasm and vacuole, and if it is assumed that absorption of a salt by plant cells consists of an interchange of kations between the external solution and the cytoplasm and an interchange of anions between the external solution and the vacuole. A certain amount of experimental data can be adduced in support of such a scheme. It may also be pointed out in passing that carbon dioxide is being constantly formed in living cells by respiration and hence there is a continuous supply of the ions of carbonic acid, so that if absorption of ions from outside the cell is a question of ionic interchange through a membrane under conditions tending towards a Donnan equilibrium fresh material for this interchange is being continually produced.

It may, then, be concluded that there is a fair amount of evidence in favour of the existence of membranes limiting the protoplasm, such

evidence being derived from a number of diverse methods of enquiry. While the evidence obtained along any one line is not in itself completely convincing, the whole body of evidence seems sufficient to justify, as a working hypothesis, the acceptance of the view that such membranes are present.

This being so we may enquire into the constitution of the membrane. Now under the Willard Gibbs principle that substances which lower the surface tension of a liquid tend to accumulate at the surface we should expect such substances present in the protoplasm to be more concentrated in the surface layer than elsewhere. We might expect particularly an accumulation here of the so-called "lipoid" substances, fats and complex fatty substances such as phospholipines, which form an essential part of the protoplasm. It is possible that in contact with substances present in the external medium permeating the cell wall such a layer might become changed not only in physical, but also in chemical constitution, and a definite membrane differing in constitution from the bulk of the protoplasm be produced; one, moreover, the permeability properties of which might be influenced by substances in contact with it.

Overton's experiments performed more than forty years ago indicated the ease with which substances soluble in fats or fat solvents entered cells, and more recent work has in general confirmed this finding. It is scarcely likely that the membrane is a homogeneous layer of fatty material, since water penetrates with ease into cells, and although Osterhout sees no difficulty in water passing through a continuous layer of fat, the theory that the cell membrane is an ultra-filter composed of a continuous phase of fat with pores of water or an aqueous medium seems to fit most of the facts relating to the capacity of various substances to enter plant cells. Such a layer must, however, be very thin. It is not visible under the highest powers of the microscope. Seifriz with the aid of a micrometer attempted to measure the thickness of the membrane which appears on protoplasm after it has been isolated and has coagulated, and estimated the thickness to be less than 0.2μ . Collander, from estimations of the rate of entry of non-electrolytes into cells of *Chara*, estimated the thickness of the membrane to be significantly less than 0.3μ . These determinations are of course not supposed to be anything more than crude estimates, but they suggest that the thickness of the plasma-membrane is of the order of 0.1μ .

To sum up, the structures in the plant cell system, which can be regarded as functioning as membranes are the cell wall, the protoplasmic layer as a whole, and the plasma-membranes which form the limiting layers of the protoplasm. The cell wall serves to give rigidity to the plant and is generally completely permeable to water and dissolved substances; only exceptionally does it play any direct part in preventing the entry of dissolved substances into cells. The protoplasm as a whole may function as a membrane determining the passage of substances from an outside medium into the central vacuole, but there is a body of evidence suggesting that the limiting layer of the protoplast, forming a thin membrane composed largely of fatty substances but with pores containing an aqueous phase, is chiefly responsible for determining the entrance or non-entrance of substances into plant cells.

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GENERAL DISCUSSION.

Dr. F. C. Steward (London) said: My comments are of two kinds: the first of a general nature, the second quite specific.

It was a surprise to read that Professor Stiles still regards the evidence for the very existence of plasma membranes as somewhat inconclusive. The evidence is described as "a fair amount of evidence" which in its "cumulative effect" only justifies the existence of membranes as "a working hypothesis." What may be described as the "morphological evidence" for the membranes which bound the protoplast seems now rather impressive. With respect to this, and also their function, micro-dissection seems to have contributed more than Professor Stiles seems willing to admit. The work of Chambers, Scarth, Seifriz, Plowe and others has demonstrated the reality of the membranes as organised structures more tangible, thicker and more stable than mere surfaces of contact between immiscible fluids. The evidence that these structures play a part in the interchange of solutes between cells and their environment is also rather impressive.

The evidence that dyes which do not penetrate cells will freely permeate the protoplasm when injected within the external membrane cannot be dismissed because the cells are "abnormal." Abnormality and injury should lead to free entry of both protoplasm and vacuole and to outward diffusion into the surrounding fluid. All the evidence indicates that micro-dissection skilfully performed does not cause drastic injury and may not even stop the normal protoplasmic streaming.

The evidence for the physical reality of the tonoplast—the wall of the vacuole of De Vries—is even more striking. An experiment of Seifriz repeated by Höfler and Chambers and by Plowe shows how the whole protoplast may be isolated from epidermal cells of *Allium*, and the manipulations by which the isolated vacuole with its vacuole membrane intact may be obtained as a structure freely suspended in water. Such vacuoles retain their contents (*e.g.* anthocyanin) and also respond by volume charges to the osmotic pressure of the external solution. This has led some to stress that the tonoplast is the seat of the osmotic properties of the cell. This kind of direct evidence cannot be ignored or lightly dismissed merely because one specialised application of micrurgy (protoplasmic viscosity determinations) has met with criticism.

Further the direct application to plant cells of the Gibb's principle is an over simplification. This principle implies reversible equilibrium between the phases concerned unrestricted by definite pellicles of the kind which, the above evidence indicates, actually exist. In view of this and the high-water content of protoplasm too much emphasis can easily be placed upon those substances, *e.g.*, lecithin which are conspicuous because of their ability to reduce the surface tension between water and air.

The following specific questions arise from Professor Stiles' reference to phenomena which are not merely properties of the membranes alone—namely the accumulation of ions. It is said that "a certain amount of evidence can be adduced in support of such a scheme"—referring to that of Briggs based upon a suggested application of the Donnan Equilibrium. What is the experimental evidence upon which Professor Stiles bases and maintains this statement in the light of the trend of recent work?

Professor Stiles points to the continuous supply of carbon dioxide in respiring cells and again suggests that the issuing H^+ and HCO_3^- ions can exchange for entering salt ions. It would be interesting to know how on this view the accumulation of ions by green cells in the light would be explained. All the direct evidence indicates that mere carbon dioxide production alone does not lead to salt accumulation.

Professor E. Gorter (Leiden) said: I should like to make a remark on the subject of the surface absorption of capillary active substances that

are introduced into a drop of water. At an interphase between air and water fatty acids and fats are all orientated in a monolayer with the polar groups turned towards the water. Between paraffin and water, fatty acids lie almost flat on the water, occupying a much larger surface per molecule. Proteins, however, as recently shown by Langmuir, show no difference when examined at the interphase air-water and paraffin-water respectively. Now at a water-water interphase one can conceive only a double layer of polar substances which turn their polar groups towards the two water-layers. The amount of lipoids present in the red blood cell is just sufficient to cover its surface with a bimolecular layer.

Professor Kurt H. Meyer (*Genthod-Geneve*) said: If the analysis of the ionic content suggests the presence of a Donnan-equilibrium (Donnan-distribution) there is no reason to assume the presence of an actual membrane. This distribution means simply that certain ions are unable to diffuse to the exterior. They may hang as lateral -COO- or -NH_3^+ ions from a network of protein-chains.¹ On the lines suggested by Briggs we can say that if, in addition to networks of acid protein—or other primary—valence chains with -COO- groups, there are present others, with basic groups (-NH_3^+), which may be neutralised by mobile cations (Na^+ , H^+ , etc.), or anions respectively, such a tissue can take up a given salt (e.g., KCl) from its surroundings, even against the concentration gradient, without an increase in free energy. The movable ions of the tissue are simply replaced by K^+ and Cl^- , so that the total concentration of K and Cl ions in the tissue at equilibrium is greater than in the solution. This accumulation must be sharply distinguished from the case frequently met in living systems, where the free energy of the system increases during the accumulation of a salt. This is only possible if some "dynamic machine" supplies the necessary free energy.

Professor W. Stiles (*Birmingham*), in reply, said: I do not agree with Dr. Steward that observations on the micro-dissection of cells provide impressive evidence in favour of the existence of plasma-membranes. Possibly the importance to be attached to such observations is a matter of personal opinion, but I cannot understand how visual observations on the effects of pushing a needle through protoplasm can provide strong evidence regarding the presence of a structure so thin as to be invisible under the highest powers of the microscope. Further, I cannot agree that the protoplasm of a cell, after this has been pierced with a needle, however skilfully, can remain normal. Nor do I agree that injury should inevitably lead to exudation of substances from the protoplasm, though undoubtedly diffusion of substances from the protoplasm does frequently take place as a result of injury. Similar considerations hold with regard to observations on isolated protoplasts and vacuoles. The material is in an abnormal state. Hence I maintain that while observations on micro-dissection supply indications of the existence of plasma-membranes, they do not by themselves provide definite evidence. The same is the case with regard to the application of the Willard Gibbs principle. It is well known that substances present in protoplasm lower the surface tension at the interface of an aqueous phase and air, but that the protoplasm in the plant cell is actually in contact with an aqueous medium. The evidence that substances such as lipoids might accumulate at the protoplasmic surface and there, probably after reacting with a constituent of an adjoining phase, form a limiting membrane, is no more conclusive than the evidence in favour of such a membrane derived from micrurgical observations.

Dr. Steward asks for the evidence in favour of Briggs's scheme. This is to be found in papers by Briggs and by Briggs and Petrie published in the years 1930 and 1931 in *Proceedings of the Royal Society*. It is there shown that experimental data regarding salt intake are consistent with the suggested scheme. It is possible that other schemes might also fit the

¹ Proctor and Wilson, *Theory of Swelling*, *J. Chem. Soc.*, 1916, 109, 307.

relatively few facts available, and my own opinion is that a vastly increased quantity of experimental data is required, both with regard to absorption of salts by non-green tissues and by the green cells in the light to which Dr. Steward refers, before any generally acceptable explanation of accumulation is likely to be put forward.

THE APPARENT PERMEABILITY OF THE CAPILLARY MEMBRANE IN MAN.

BY ANCEL KEYS.

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It is generally assumed that the blood vascular capillary membranes are completely and readily permeable to all substances of less than colloidal, or at most, infra-colloidal, dimensions. Krogh,¹ stated (p. 281), "The osmotic pressure of the crystalloids cannot become *effective* in normal capillaries, because their walls are permeable to these substances which will pass through by diffusion until an equilibrium is established." Further (p. 278), "There is no trustworthy evidence of the capillaries having any power of hindering or favouring the passage by diffusion of all kinds of crystalloids through the endothelium."

The underlying thought in these statements is that the capillaries do not *actively* influence the exchanges across their membranes and that the final equilibrium is the result of purely passive exchanges of both water and crystalloids. There is no reason to doubt either of these contentions. It does not follow, however, that the different crystalloids penetrate the capillary membrane at equal rates nor that, in normal life, equilibrium or "steady state" conditions are invariably established.

Stated in this way, it is improbable that any one would defend either of these last two theses though much physiological reasoning appears to have accepted them implicitly. Krogh² (p. 278), however, has recognised that "The rates at which different substances will diffuse through the capillary wall seem to be closely related to their rates of free diffusion in water or gelatine." Unfortunately, the evidence from Clark³ and others in support of this statement is not strictly pertinent, because other membranes than the capillary wall are probably the limiting factors in their experiments.

The points I wish to emphasise in this paper are: (1) the capillary membrane offers an appreciable resistance to the passage of crystalloid ions and molecules, (2) in normal life, alterations of functional activity are frequently so rapid as to preclude the establishment of final equilibrium conditions, and (3) the non-equilibrium distribution of diffusible substances between blood and tissue are of importance to the organism.

Direct measurement of the water and crystalloid permeability of the capillary membrane under physiological conditions would be difficult if not impossible. However, valid conclusions may be drawn from

¹ Krogh, A., *Anatomy and Physiology of Capillaries* (revised edition, 1929. Yale Univ. Press, New Haven).

² Krogh, A., *Anatomy and Physiology of Capillaries*, 1922. (Yale Univ. Press, New Haven.)

³ Clark, A. J., *J. Pharm. Exp. Therap.*, 1921, 16, 415.

indirect studies. In almost all cases the experimental evidence can only decide whether the exchanges between blood and tissue (interstitial) fluid proceed at different rates. These exchanges involve two processes: (1) the exchange across the capillary wall, and (2) the diffusion and distribution throughout the tissue fluid.

Differences in the total rates of exchange may, of course, be partly or even entirely due to differences in the rates in the second process, but this could only be the case if the time required for the diffusion and distribution in the tissue fluid is very long as compared with the time needed for the exchange across the capillary wall. This seems unlikely in view of the facts that the distances for diffusion (distances between capillaries) are very small, and that the tissue fluid is not without a circulation of its own. In the latter connection there are: (1) the peri-capillary circulation from the arterial to the venous end of the capillary,⁴ (2) the lymphatic circulation, (3) the agitation of muscular contractions, (4) arterial pressure pulses and "looping" of the arterioles,⁵ (5) alterations of the capillary bed itself,² and (6) the stirring effect of the diffusion gradients incidental to energy metabolism of the tissue cell.

The distinction between exchange across the capillary wall and the exchange between blood plasma and tissue fluid is theoretically important, but it may be disregarded in many physiological enquiries. Having recognised the uncertainties as to the ultimate limiting factors, we may analyse the available evidence on the relative rates of exchange of various substances between the plasma and the tissue fluid.

Evidence from Intravenous Injections.

It is unnecessary to discuss the frequent statements to the effect that crystalloids such as calcium and sugar pass readily and rapidly from blood to tissue fluid.⁶ By "rapidly," these authors usually mean something like an hour or more. There are many incidental observations which indicate that water and various crystalloids penetrate the capillary membrane at quite different rates and occasional authors⁷ have suggested that the resistance of the capillary wall to the passage of crystalloids may be of importance, but on the whole the question has been neglected.

Intravenous injections of calcium,⁸ sulphate,⁹ magnesium,¹⁰ and phosphate,¹¹ produce a temporary rise (up to 1 to 2 hours) in the plasma concentration of these substances; the magnitude of this change is more

⁴ (a) Schade, H., and Claussen, F., *Z. klin. Med.*, 1924, **100**, 363. (b) Starling, E. H., *J. Physiol.*, 1896, **19**, 312.

⁵ Swindle, P. F., *Amer. J. Physiol.*, 1933, **106**, 95, 105.

⁶ E.g. (a) Arnold, R. M. and Mendel, L. B., *J. Biol. Chem.*, 1927, **72**, 189.

(b) Kurokawa, T., *Tohoku J. Exp. Med.*, 1928, **10**, 64.

⁷ Roth, W., *Arch. Anat. Physiol., Physiol. Abt.*, 1899, p. 416.

⁸ (a) Clark, G. W., *J. Biol. Chem.*, 1920, **43**, 89. (b) Jansen, W. H., *Deut. Arch. klin. Med.*, 1924, **144**, 14; **145**, 209. (c) Dadlez, J., *Biochem. Z.*, 1926, **171**, 146. (d) Brull, L., *Arch. Internat. Physiol.*, 1930, **32**, 130. (e) Greville, G. D., *Biochem. J.*, 1931, **25**, 1931.

⁹ (a) Meyer-Bisch, R., *Biochem. Z.*, 1924, **150**, 23. (b) Denis, W. and Leche, S., *J. Biol. Chem.*, 1925, **65**, 565. (c) Bourdillon, J. and Laviertes, P. H., *J. Clin. Investig.*, 1936, **15**, 301.

¹⁰ (a) Láng, S., and Rigó, L., *Arch. exp. Path. Pharm.*, 1929, **139**, 1. (b) Taylor, W. F., and Winter, J. E., *J. Pharm. Exp. Therap.*, 1929, **35**, 435. (c) Schmidt, C. L. A., and Greenberg, D. M., *Physiol. Rev.*, 1935, **15**, 297, citing Greenberg and Tufts.

¹¹ Binger, C., *J. Pharm. Exp. Therap.*, 1917, **10**, 105.

than would be expected if the injected salts were equally distributed between the water of the blood plasma and that of the tissue fluid. When fairly large amounts of these substances are injected, marked haemodilution over and above the expected volume change may be produced.¹² This last phenomenon may also be produced by the injection of hypertonic NaCl, urea, and sugar solutions and even by the injection of *isotonic* sucrose.¹³

The attempts to measure the total volume of extracellular fluids in the body by the introduction of measured amounts of sucrose, sulphocyanate or sulphate¹⁴ provide interesting evidence. These authors apparently believe that the distribution between plasma and tissue fluid of these substances by diffusion from the capillaries is complete before two or three hours but is not complete in one hour. Moreover, there are differences between these substances. "Of the three substances employed SCN is distributed through the body most rapidly, sucrose least rapidly" (*op. cit.*¹⁴, p. 266).

More exact calculations can be made from the data on sulphate injections given by Bourdillon and Lavietes.⁹ After small injections of sulphate in man (about 0.5 m. Eq. per kg. body weight), equilibration of SO₄ requires at least an hour, though osmotic readjustment by shift of water is accomplished in a much shorter period of time. With large injections (2 or 3 m. Eq. of SO₄ per kg.), marked haemodilution occurs and persists for an hour or more. The extent of this haemodilution can only mean that sulphate exchange lags behind the water shift for at least an hour.

Studies on the fate of sucrose intravenously injected in man¹⁵ show strikingly the fact that osmotic equilibration by a shift of water takes place from three to ten times as fast as sucrose exchange.

The effect of sugar solutions in dehydrating tissues and hydrating the blood has been much used for the reduction of intracranial pressure; in these cases the hydræmia resulting from the sugar injection far exceeds the volume of water that is extracted from the brain.^{13, 16} These actions depend, of course, on the fact that the limiting membranes involved permit the passage of water much more readily than the passage of the sugar molecules. When one compares the effect of these solutes on muscle with the effect on the brain, it appears that at least some of the difference, with regard to permeability, between the capillary membranes and the meninges is only quantitative and not qualitative.¹⁷

The exchanges resulting from intravenous administration of salt and sugar solutions are complex and, when substances foreign to the body are introduced, may be "unphysiological." Bromide introduced into the blood is irregularly distributed in a way which could be taken to indicate a higher mobility in the body than chloride;¹⁸ this would be in agreement with the findings of Risse¹⁹ with gelatin filters. More physiological conditions are met with in the transudation resulting from experiments on posture and exercise.

¹² Odaira, T., *Tohoku J. Exp. Med.*, 1923, 4, 523.

¹³ (a) Lazarus-Barlow, W. S., *J. Physiol.*, 1895, 19, 437. (b) Smith, H. P., *Bull. Johns Hopkins Hosp.*, 1925, 37, 177. Kinsman, J. M., Spurling, R. G., and Jelsma, F., *Amer. J. Physiol.*, 1928, 84, 165.

¹⁴ Lavietes, P. H., Bourdillon, J., and Klinghoffer, K. A., *J. Clin. Investig.*, 1936, 15, 261.

¹⁵ Power, M. H., and Keith, N., *Unpublished studies*.

¹⁶ (a) Weed, L. H., and McKibben, P. S., *Amer. J. Physiol.*, 1919, 48, 512, 530. (b) Foley, F. E. B., and Putnam, T. J., *Amer. J. Physiol.*, 1920, 53, 464. (c) Bullock, L. T., Gregersen, M. I., and Kinney, R., *Amer. J. Physiol.*, 1935, 112, 82.

¹⁷ Cf. e.g. Baer, R., *Arch. exp. Path. Pharm.*, 1926, 119, 102.

¹⁸ Hastings, A. B., and Van Dyke, H. B., *J. Biol. Chem.*, 1928, 78, xxv.

¹⁹ Risse, O., *Pflüger's Arch.*, 1926, 212, 375.

Evidence from Studies on Posture and Exercise.

Quiet standing results in decreased blood volume and increased plasma protein concentration due to filtration into the tissue spaces of the legs.²⁰ Not only proteins, but lipid phosphorus, fatty acids, and cholesterol are apparently restrained by the capillary wall in experiments of this type.²¹

In human subjects brief severe work produces increases in haemoglobin and plasma protein concentrations which are largely, if not entirely, the result of filtration of water into the tissues.²² Immediately following running to exhaustion in one minute, as much as 24 per cent. of the water of the plasma may have been lost to the tissues and during the exercise a transudation rate as high as 500 c.c. or more a minute may be seen. Does this fluid constitute a simple ultrafiltrate from the plasma?

In the first place, it seems probable that the transudate is not protein free. Though the plasma protein concentration rises markedly as a result of the exercise, the colloidal osmotic pressure either decreases or does not increase, even when all Donnan and salt effects are eliminated.²² Either proteins of small molecular weight (and high osmotic activity) are lost with the water, or we must make the improbable assumption that they are destroyed in the blood in the brief space of one minute. One can calculate the protein loss within the limits of reasonable possibilities; the protein concentration of the transudate would appear to be something like 0.2 to 1.0 per cent.

This protein loss would seem to be a serious reduction of the force available to cause a restoration of the blood volume to normal. This is more than offset by the fact that, under these conditions, the *whole* of the plasma calcium appears to be as indiffusible as protein.²³ The increase in effective osmotic pressure due to the restraint by the capillary wall of the so-called "diffusible" calcium (*i.e.*, that part not bound to protein) is of the order of 30 to 60 mm. of water, or from 10 to 20 per cent. of the total colloidal osmotic pressure.

Preliminary experiments of the same kind indicate that the inability of Ca^{++} to pass the capillary wall quickly may be shared by sulphate and magnesium. These effects are transient to be sure, but they are very marked for some minutes and may be discerned as long as the restoration of the blood volume is in progress, *i.e.*, for about an hour.

In the light of earlier work the resistance of the capillary membrane to sudden exchanges of difficultly diffusible molecules like Ca^{++} is surprising chiefly because of its completeness. When we pass to a substance like sodium the expectation might be different.

The immediate effect of brief exhausting exercise is a rise in plasma sodium concentration of from 3 to 10 per cent., *i.e.*, from a fifth to a third the relative rise in plasma protein or calcium. There is no conceivable reservoir, inside or outside the blood, from which this sodium could come and there is not the slightest reason to doubt that the rise in $[\text{Na}]$, is simply a reflection of the fact that sodium passes through the capillary wall at a rate very appreciably slower than does water but still much faster than calcium or protein.

²⁰ (a) Thompson, W. O., Thompson, P. K., and Dailey, M. E., *J. Clin. Invest.*, 1928, **5**, 573. (b) Waterfield, R. L., *J. Physiol.*, 1931, **72**, 110, 121.

²¹ Man, E. B., and Peters, J. P., *J. Clin. Invest.*, 1933, **12**, 1031.

²² (a) Dill, D. B., Talbott, J. H., and Edwards, H. T., *J. Physiol.*, 1930, **69**, 267. (b) Keys, A., *J. Biol. Chem.*, 1934, **105**, xlv. (c) Keys, A., and Taylor, H., *J. Biol. Chem.*, 1935, **109**, 55.

²³ Keys, A. and Adelson, L., *Amer. J. Physiol.*, 1936, **115**, 539.

The value of $[Na]_s$ in recovery is in harmony with this view. The return to the resting level of $[Na]_s$ follows a curve similar in form to that for the blood volume, plasma protein, and calcium, but is complete in twenty to thirty minutes. The behaviour of chloride, after correcting so far as possible for exchanges with the red cells and the secondary effects of acidosis and high CO_2 concentration, seems to resemble that of sodium.

The intravenous injection of adrenalin produces a transient haemo-concentration and transudation not unlike that of exercise, but without the complication of osmotic changes in the muscle cells. Again the effect on the $[Na]_s$ is an immediate small rise. The same explanation should suffice for both the adrenalin and the exercise results and the conclusion is that, in both cases, the transudate contains, at first, less sodium than would an ultra-filtrate.

The behaviour of potassium is much more complex.²⁴ The immediate effect of the brief exercise is to produce a marked rise, up to 25 per cent. above rest, in $[K]_s$. This is considerably more than could possibly be accounted for on the basis of simple retardation of filtration through the capillary membrane. Within three to eight minutes the $[K]_s$ falls to a value significantly lower than in rest; thereafter $[K]_s$ rises slowly to an abnormal level (up to 15 per cent. above rest), and then gradually subsides to normal. Exchanges with the red cells, which contain relatively much potassium, cannot explain this cycle. Obviously changes other than simple transudation dominate the picture. The concentration gradients existing in these experiments are unknown, but the changes in $[K]_s$ must involve large exchanges across the membrane. One can only conclude, in the present connection, that the capillary membrane must be fairly readily permeable to potassium.

The results of adrenalin injections include marked changes in $[K]_s$, but again simple transudation plays only a subordinate rôle. However, the rapidity of the changes in these experiments likewise suggests that potassium diffuses across the capillary wall with relative ease.

The Order of Diffusion Rates.

Summing up the available evidence, the approximate rates of diffusion across the capillary wall in man seem to be :

$H_2O > Urea > K^+, Na^+, Cl^-, NO_3^- > Ca^{++}, Mg^{++}, \text{phosphate} > \text{glucose}, SO_4^{--}, SCN^- > \text{sucrose}.$

This order may be compared with the rates of filtration of diffusion through artificial membranes. According to Risse¹⁹ the order for gelatin filters runs :

$H_2O > NH_4^+ > Br^- > Cl^-, K^+, Na^+, NO_3^-, SCN^- > Li^+, Ca^{++}, Mg^{++}, \text{phosphate} > SO_4^{--}.$ Teorell²⁵ has made measurements of mobility ratios of the monovalent kations in cellophane with the following result : $H^+ > NH_4^+ > K^+ > Na^+ > Li^+.$ I have made measurements of diffusion rates across cellophane membranes (Dupont nos. 300 and 600). The order found was : $H_2O > Cl^-, Na^+, K^+ > Ca^{++}, \text{glucose} > SO_4^{--}, \text{sucrose}.$ Similar results are obtained with collodion membranes.

So far as can be seen at present, the rates of diffusion of crystalloids across the capillary membrane run more or less parallel to the abilities

²⁴ Keys, A., *Science*, 1937, **85**, 317.

²⁵ Teorell, T., *J. Gen. Physiol.*, 1936, **19**, 917.

of these substances to penetrate artificial membranes like gelatin, cellophane and collodion. The only serious discrepancy is with regard to sulphocyanate. The apparent abnormality of sulphocyanate, however, may be the result of a tendency to form a complex with protein.¹⁴

The question as to the colloid (protein) permeability of the capillary membrane has been discussed at length by Krogh,¹ Conklin,²⁶ Drinker and Field,²⁷ Landis,²⁸ Keys and Taylor,²² and others. The evidence is overwhelmingly in favour of the conclusion that the capillaries are not completely "protein tight," and that the protein concentration of transudates is ordinarily something like 0.5 to 1 gm. per 100 c.c.

The Nature of the Capillary Membrane.

The picture of the physical nature of the capillary membrane must be reconciled with all the foregoing facts. Differences in the diffusion rates between glucose and maltose, or between glycol and glycerol, can be demonstrated with extremely permeable ("kuprophan") membranes,²⁹ but, in general, artificial membranes which allow the escape of proteins are so permeable that differential diffusion of crystalloids is not easy to prove.

The most reasonable explanation for all the facts stated here would be to assume that the capillary wall does not comprise a uniform barrier, but has occasional "holes" or regions of excessive permeability. Field and Drinker³⁰ have observed the passage of graphite and calcite particles, of about 1μ in diameter, across the capillary walls in the tongue, the mesentery, and the web of the frog and have traced the passage of such particles to the lymphatics in both the frog and the unanæsthetised dog. They also note that in the diapedesis of red cells no unusual escape of plasma proteins accompanies the erythrocytes.

The theory of the existence of "holes" in the capillary membrane would, of course, explain the fact that in exercise the membrane leaks no more calcium than it does protein. It is not necessary to conceive of permanent gaps in the continuity of the capillary membrane; rather one might expect that holes or areas of excessive permeability are transient and tend to appear more frequently when the capillary is asphyxiated or otherwise damaged.

On this theory the properties of the "intact" part of the capillary wall are not remarkable; the comparison with an artificial membrane like "kuprophan" or thin collodion becomes more exact.

Discussions of the capillary membrane always emphasise its extreme permeability. It is a commonly expressed opinion that this permeability so far exceeds that of artificial membranes that comparison cannot be made. A few simple calculations will expose the fallacy of this view.

The filtration rate through the capillary membrane³¹ works out to be 370 cubic micra per square micron of surface per minute under a pressure of 1 atmosphere, or $0.037 \text{ c.c. per cm.}^2 \times \text{min.} \times \text{atm.}$ Using Krogh's² estimate of something like 6000 sq. m. of capillary surface in a good-sized

²⁶ Conklin, R. E., *Amer. J. Physiol.*, 1930, **95**, 98; 1935, **112**, 401.

²⁷ Drinker, C. K., and Field, M. E., *Lymphatics, Lymph and Tissue Fluid*, 1933 (Williams and Wilkins, Baltimore).

²⁸ Landis, E. M., *Physiol. Rev.*, 1934, **14**, 404.

²⁹ Brintzinger, H., and Osswald, H., *Kolloidchem. Z.*, 1935, **70**, 198.

³⁰ Field, M. E., and Drinker, C. K., *Amer. J. Physiol.*, 1936, **116**, 597.

³¹ Landis, E. M., *Amer. J. Physiol.*, 1927.

man, the potential filtration rate is enormous, 2200 liters per atmosphere per minute in a man of 75 kg. body weight. Actually, of course, this limiting rate could only be attained in an extremely limited area. We have been able, in normal man, to reach a rate of filtration out of the blood stream of 600 c.c. per minute (for about one minute in the most violent exercise), and a filtration into the blood stream of 800 c.c. per minute (for about $1\frac{1}{2}$ minutes after intra-arterial injection of hypertonic sucrose). Other things being equal, this would indicate maximum effective filtration pressures of the order of 0.003 atmosphere or only about 3 mm. H_2O .

Comparison may be made with the rates of filtration through artificial membranes. Using the most uniform collodion membranes with the highest permeability that will still retain protein, I have frequently obtained 6 c.c. per hour with a filtering surface of 4 sq. cm. under a pressure of 3 atmospheres. This amounts to 0.008 c.c. per $cm.^2 \times min. \times atm.$, or between one-fourth and one-fifth the rate estimated for the capillary wall of the frog's mesentery.

Manegold's³² careful studies of collodion membranes provide a valuable comparison. With the technique of Bjerrum and Manegold,³³ collodion membranes of calculated mean pore radius from 1.5 to 50 $m\mu$ (10^{-7} cm.) can be prepared. This compares closely with the total range of radii of all kinds of colloids (considered as spheres), which is often given as 0.5 to 50 $m\mu$. The properties of some of these membranes are given in Table I.

TABLE I.—COMPARISON OF THE PERMEABILITY OF MEMBRANES.*

Membrane.	Thickness in Microns. (δ).	Mean Pore Radius in $m\mu$ ($=10^{-7}$ cm.)	Permeability, P , in c.c. per min. $\times cm.^2 \times atm.$	Specific Permeability, $P \times \delta \times \eta$.
Manegold No. 116 .	52	1.56	0.00003	0.000018
" " 121 .	113	5.9	0.0050	0.00604
" " 111 .	180	10.9	0.0118	0.0232
" " 103 .	370	20.0	0.0208	0.091
" " 201 .	426	33.2	0.0542	0.246
" " 206 .	518	48.0	0.0980	0.543
Frog capillary .	? 0.2 to 2	0.7 to 2.1	0.0370	0.000061 to 0.00061

* Data from Manegold (1929) for collodion, from Landis (1927) for capillary membrane. Permeability (P) measured as c.c. H_2O filtered through 1 $cm.^2$ per minute at 1 atmosphere pressure. Mean pore radius for capillary calculated

by equation of Bjerrum and Manegold (1927): r (in $m\mu$) = $\sqrt{8P' \cdot \delta \cdot \eta \cdot \frac{3}{W}}$ where P' is permeability measured in c.c. per second $\times cm.^2 \times cm.$ H_2O , δ = membrane thickness in microns, η = coeff. of viscosity in c.g.s. units (here about 0.011), and W = gm. H_2O per c.c. of membrane (assume 0.7 for frog capillary).

Another method of calculation may be used with the data of Krogh, Landis and Turner.³⁴ They reported that a change in pressure from 17 to 48 cm. H_2O on the human forearm produced a filtration rate out of the blood of 0.070 c.c. per minute per 100 c.c. of arm. Assuming 70 per cent. of the forearm to be muscle, this would correspond to 329 c.c. per minute in 1 kg. of muscle under a pressure of 1 atmosphere. Using Krogh's estimate of 120 sq. m. of capillary surface per kg. of muscle, the permeability works out to be 0.000274 c.c./min. $\times cm.^2 \times atm.$

³² Manegold, E., and Hofmann, R., *Kolloid-Z.*, 1930, 50, 22.

³³ Bjerrum, N., and Manegold, E., *Kolloid-Z.*, 1927, 42, 97; 43, 5.

³⁴ Krogh, A., Landis, E. M., and Turner, A. H., *J. Clin. Investig.*, 1932, 11, 63.

The disparity between this value and that calculated for the single frog capillary wall is enormous; apparently other factors are at work. Many of the capillaries may be collapsed by the pressure and the surface would be over-estimated accordingly. Only a part of the pressure can be effective because it is applied generally; the net filtration pressure is uncertain. Finally, in any large mass of tissue, as soon as filtration begins the crystalloids left behind by the rapid filtration of water out of the blood will exert a powerful counter osmotic pressure.

It seems as though the only property of the capillary membrane which is obviously remarkable is its thinness; otherwise it merely looks like a rather impermeable membrane. Note that the calculated mean pore radius is something like 0.7 to 2.1 $m\mu$; that is, appreciably less than the radius of colloid molecules like albumin and hæmoglobin.³⁵

Anomalies in Initial Exchanges.

The study of non-equilibrium systems has not progressed far enough to permit much more than speculation about the phenomena at the capillary membrane during changes in functional activity. Lazarus-Barlow¹⁸ first showed that the initial exchanges across artificial membranes may set up unexpected osmotic forces. Höber³⁶ found marked effects from which he concluded (p. 229): "*Eine osmotische Druckdifferenz eintritt bei einer Verschiedenheit der Diffusionsgeschwindigkeit, dass der osmotische Druck erhöht sich auf der Seite der trennenden Wand, wo sich die Lösung der langsamer diffundirenden Verbindung befindet, und dass die Druckdifferenz um so grösser ausfällt, je verschiedener die grösse der Diffusionskoeffizienten.*"

There is no reason to believe that similar phenomena do not take place at the capillary wall. There is much more doubt about the negative osmosis studied by Jacques Loeb and the initial ion accumulation observed by Teorell.³⁷ The remarkable effects on the initial exchanges (five to twenty minutes) of surface active substances like sodium oleate or glycocholate³⁸ deserve more study. Brinkmann and Szent-Györgi³⁹ reported that surface active substances may greatly alter the colloid permeability of collodion membranes without changing the water permeability.

Waelsch, Kittel and Busztin,⁴⁰ have reported some surprising rhythmic alterations of concentration in membrane and colloid systems. It is impossible to say what, if any, rôle this phenomenon plays in the living organism.

Physiological Significance.

It is difficult to evaluate, in general terms, the physiological significance of the facts which have been discussed in this paper. In the course of normal life there are a host of factors altering concentrations and osmotic relations in the body. Readjustments, tendencies to establish new equilibria, exchanges of water and solutes in both directions across the capillary membrane, are constantly taking place at varying rates and in varying locations. Only the grossest of these phenomena are susceptible of study at present.

³⁵ Cf. e.g., Northrop, J. H., and Anson, M. L., *J. Gen. Physiol.*, 1929, 12, 543.

³⁶ Höber, R., *Pflüger's Arch.*, 1899, 74, 224.

³⁷ Teorell, T., *J. Physiol.*, 1933, 78, 11 (*Proc. Physiol. Soc.*).

³⁸ Ederer, S. A. P., *Proc. Soc. Exp. Biol. Med.*, 1925, 23, 66.

³⁹ Brinkmann, R., and Szent-Györgi, A., *Biochem. Z.*, 1923, 139, 261, 270.

⁴⁰ Waelsch, H., and Kittel, S., *Kolloid-Z.*, 1936, 76, 19. Waelsch, H., Kittel, S., and Busztin, A., *Z. physiol. Chem.*, 1935, 234, 27; *Kolloid-Z.*, 1936, 74, 22.

Krogh has convinced us that at any one time the bulk of the blood is in the capillary system and not in the impermeable and structurally substantial venous and arterial systems. It would seem almost miraculous that the blood volume is not constantly subject to enormous and fatal variations. The contraction of the muscles, changes in posture, ingestion of food or drink, all provide osmotic and hydrostatic forces theoretically sufficient to upset completely the balance of fluid between blood and tissue. Prompt and powerful compensation is needed to maintain homeostasis.

The compensatory and regulatory mechanisms are numerous and many investigations have been concerned with the heart rate and stroke volume, the changes in the vascular bed, the rôle of the carotid sinus, the valves of the veins, the contraction of the capillaries, etc. The compensatory effects in the blood tissue exchanges themselves, however, have been generally overlooked.

The events in exercise illustrate the point well. Ranke⁴¹ first showed that the osmotic pressure of a muscle is increased when it is exercised. This change is due to the formation of many small molecules and ions from large complexes. Meyerhof⁴² found an average rise in osmotic pressure of between 1 and 2 atmospheres in exercised frog muscle. Unrestrained, a force of much less than this amount would almost instantly empty the blood stream of all water. Actually, the muscle does swell but the changes are relatively small.⁴³

The first restraint is the fact that even water requires some time to cross the capillary membrane. Secondly, some of the new ions (e.g. lactic acid) begin to diffuse into the blood from the muscle thereby reducing the gradients. The osmotic pressure of the blood rises and only a part of this can be accounted for on the basis of new ions from the tissues.⁴⁴ As I have shown in the discussion of my exercise experiments, the plasma crystalloids are markedly restrained from filtering out of the blood stream with the water which is drawn to the muscles. The retention of these crystalloids provides a powerful force to prevent undue reduction in the plasma volume. I have ventured to term this action "osmotic buffering."

It must be granted that osmotic buffering comes into play whenever there is a sudden shift from equilibrium conditions, and the greater the stress the greater the compensatory action. In the most rapid disturbances, Na^+ and Cl^- , because of their high concentration, must play a major rôle; in less rapid alterations, ions like Ca^{++} , SO_4^{--} , and probably amino acids, glucose, etc., would bear the brunt. It should be noted that, if the foregoing argument be granted, damage to the capillary walls so slight as to allow very little protein loss, could still have unfortunate results owing to a reduction in the potential osmotic buffer force.

Summary and Conclusions.

Exercise, change of posture, ingestion of food or drink, and circulatory alterations, all provide forces far greater than would be needed to cause

⁴¹ Ranke, J., *Tetanus* (Engelmann, Leipzig, 1865).

⁴² Meyerhof, O., *Biochem. Z.*, 1930, **226**, 1.

⁴³ (a) Barcroft, J., and Kato, T., *Proc. Roy. Soc., B.*, 1915, **88**, 541. (b) Cohnstein, J., and Zuntz, N., *Pflüger's Arch.*, 1888, **42**, 303.

⁴⁴ (a) Margaria, R., *J. Physiol.*, 1930, **70**, 417. (b) Hill, A. V., *Adventures in Biophysics* (Oxford University Press), 1931. (c) Covián, F. G., and Krogh, A., *Skand. Arch. Physiol.*, 1935, **71**, 251.

fatal changes in the volume of blood in the vascular system. This danger is prevented by a variety of compensatory forces, of which osmotic buffering is not unimportant.

Osmotic buffering has its origin in the fact that water and various crystalloids do not diffuse through the capillary wall at identical rates. Although the capillary wall is passively and completely permeable to these substances, it is necessary to add that, whenever functional or experimental states alter the osmotic balance between blood and tissue, readjustment tends to take place by a shift of water and only secondarily by a shift of solutes. The shift of water, however, sets up opposing osmotic forces.

The order of the rates of diffusion across the capillary membrane in man is, approximately :

$\text{H}_2\text{O} > \text{Urea} > \text{K}^+, \text{Na}^+, \text{Cl}^-, \text{NO}_3^- > \text{Ca}^{++}, \text{Mg}^{++}, \text{phosphate} > \text{glucose}, \text{SO}_4^{--}, \text{SCN}^- > \text{sucrose}.$

The most reasonable picture of the capillary membrane is that it behaves in most respects precisely like a simple collodion membrane with pores generally less than 2×10^{-7} cm. in radius, but having occasional "holes" at least several times this size.

In the exchanges between blood and tissue the chief limiting factor is the capillary membrane, and only rarely does the diffusion and circulation in the tissue fluid constitute an important limitation.

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GENERAL DISCUSSION.

Professor A. Krogh (Copenhagen) (communicated) : Keys discusses the exchange only as taking place between the blood and the interstitial tissue fluid, but the exchange with tissue cells is often more important.

What is called "filtration of water into tissues" during muscular work is really an uptake of water and probably an exchange of other substances by the working muscle cells. I admit that the change in colloid osmotic pressure is difficult to explain, but a change in the state of aggregation of the plasma proteins does not seem out of the question. On the whole conditions are too complicated for analysis.

In discussing the results of Krogh, Landis and Turner on filtration in the human forearm the mistake is made of assuming the filtration to take place into the muscles, whereas it is mainly subcutaneous, and the calculation of capillary surfaces comes out much too high for the reason, also, that most of the capillaries would be closed.

As stated in my paper fluid movements by filtration and osmosis take place in bulk and comprise all substances which will pass the wall; they are essentially different from diffusion of single particles.

Dr. T. Teorell (Uppsala) said: In connection with Field's and Drinker's cited observations of the passage of graphite particles across capillary walls, some points are worth mentioning. The particles were obviously capable of penetration, but the experiment gave no explanation of the forces pushing them through. There is always a possibility that the passage of a substance is a pure filtration caused by differences in hydrostatic pressure. But frequently no simultaneous migration of the water can be observed in biological phenomena of unidirectional migration. Thus we have to concentrate on the nature of the driving forces pulling the particles through the membrane.

In a general way, it seems that only two kinds of forces are of significance in biological systems; "osmotic" forces (*i.e.*, concentration gradients) and an *electrical potential gradient* (which may be present within

the diffusion boundary or membrane across which the substance has to pass). These two forces will operate simultaneously on any particle present within the membrane, taking the term particle to include ions, molecules, colloid particles or even large suspended particles up to the size of leukocytes. The electrical force influences only electrically charged particles, but most things in biology seem to carry a charge, even leukocytes. If a substance is not charged, nature tends to charge it by an appropriate transformation or complex formation, *e.g.*, phosphorylation in the case of glucose, combination with bile acids in the case of fatty substances, etc.

The passage of graphite particles across capillary walls may be explained as follows: The pure diffusion tendency of the large graphite micellæ due to a concentration gradient was certainly very weak, as is generally the case with colloids or suspensions. Accordingly, in this particular case, the "osmotic" force can be neglected as a driving factor. On the other hand an electrical force, if present, is probably important, because of the comparatively high number of charges carried by the colloid particles. Quantitatively the rate of transport across a unit cross-section of the membrane (the "flux") is defined by the expression

flux of a substance = mobility \times conc. \times force

$$\frac{dN}{dt} = u \times C \times \left(\underbrace{\frac{RT}{C} \frac{dC}{dx}}_{\text{osm.}} \pm \underbrace{\epsilon F \frac{d\pi}{dx}}_{\text{electr.}} \right)$$

where C denotes concentration, N the number of particles, u the mobility, ϵ the charge or valency, x distance in the diffusion layer, π the potential and R , T and F are the gas constant, absolute temperature and one Faraday respectively. This is the fundamental expression utilised by Nernst and by Planck in their theories for diffusion potentials. It has also recently been used in the derivation of a theory for the ionic distribution in systems where a steady diffusion takes place.¹

The flow of the substance tends to continue until a final steady state is attained, thus producing a flow *against* the concentration gradient. The ultimate steady state will be attained when the "osmotic" and electrical force balance each other, or

$$\frac{RT}{C} \frac{dC}{dx} = \pm \epsilon \cdot F \frac{d\pi}{dx}$$

and after integration

$$\log \frac{C_i}{C_o} = \pm \frac{\epsilon}{58} \cdot \pi$$

(C_i and C_o concentration inside and outside).

As a numerical illustration, assume that the average net charge carried by the graphite micelles is -5.8 and the membrane potential within the capillary wall is -10 millivolts, then

$$\log \frac{C_i}{C_o} = \frac{5.8}{58} \times 10 \quad \text{and} \quad \frac{C_i}{C_o} = 10.$$

There will be a pronounced tendency for the graphite particles to migrate across the boundary wall, since in equilibrium there should not be the same concentrations on the two sides of the wall, but instead a 10-fold difference. Not only will there be a rapid penetration but also an accumulation of the graphite particles, caused by the comparatively small P.D. of -10 millivolts!

To support this theory the following experiment was carried out: A large volume (outside) of a colloidal gum mastic suspension was separated from a *small* cell (inside) by a porous membrane (porous glass or even filter

¹ *Proc. Nat. Acad. Sci., Wash.*, 1935, **21**, 152.

paper). In the cell NaOH was added continuously so as to maintain a constant concentration gradient directed outwards (0.1 — 0.01 N.). Initially, the cell contained no mastic particles, but very rapidly they migrated inwards and accumulated in the cell to such an extent that when a steady state was reached, the small cell showed roughly a 16-fold accumulation of gum mastic particles.

In this experiment *the membrane potential performed work*. The membrane potential in this case was chiefly a diffusion potential produced by the outward diffusing NaOH (its value was 20 mv.). The reason for the electrical potential is the *difference in the mobility* between the Na and OH ions. Incidentally, the particle charge could be calculated from these results, it was 3.3. Strictly speaking, the distribution phenomenon here observed is best interpreted in terms of exchange of ions or charges owing to differences in concentration and mobility of the components in the system. It is convenient, however, to explain accumulation or impoverishment of the particles as produced by an electrical potential gradient. Similar distribution effects have been obtained with ions and proteins, *cf.* pp. 983 and 1141. It should again be emphasised that no current flows in these systems. Therefore the effect was not an electrophoretic phenomenon of the type suggested by Abramson.²

One may perhaps generalise as follows: The equilibrium towards which a species of charged particles tends may be expressed by:

electrical work = "osmotic" work

$$\epsilon \cdot F \cdot \pi \quad RT \cdot \ln \frac{C_i}{C_o}$$

$$\left(i.e., \frac{C_i}{C_o} = e^{\frac{\epsilon \pi}{RT|F|}} \right)$$

regardless of the origin of the membrane potential and the nature of the particles and the membrane. In this equation, however, other forms of energy are disregarded, as heat dissipation or surface energy, and activity concept, etc., are neglected. Obviously, therefore, the suggested expression only can give information as to the possible *maximum* distribution ratio in terms of total membrane P.D. and particle charge.

Thus, the presence of an electrical potential may provide a mechanism which can produce accumulation or the reverse. We ask, however:

(1) What is the origin of the membrane potential and how can it be kept unpolarised. Or, in other words, whence does the energy come for the maintenance of this state?

(2) What determines the "mobility" of the particles in the membrane?

Mr. O. Gatty (Cambridge) said: In addition to the osmotic and electrophoretic forces suggested by Dr. Teorell there may be another force, operating on microscopic particles, *i.e.* a reaction which continuously produces a surface active substance at one end of the particle which then moves, owing to the difference in surface tension at its two ends. The dissolution of camphor produces the well-known camphor boat and it is possible that enzymes adsorbed on one side of a body might be responsible for reactions leading to mitotic movements. Another possible set of forces arises from differences of hydrostatic pressure due to movements which might arise from streaming, muscular contractions or swelling.

Also the electrostatic forces discussed by Dr. Teorell will not distinguish between one univalent cation and another, and so additional factors have to be considered when attempting to explain the different behaviour of sodium and potassium. Dr. Teorell's diffusions always tend toward equalisation of the electrochemical potentials of ions throughout the system; this equality probably does not hold simultaneously for Na⁺ and K⁺ in biological systems showing K⁺ accumulation.³

² *Symp. Quant. Biol.*, Vol. I. (Cold Spring Harbor), 1933, p. 92.

³ For the possibility of "bound" or precipitated cations owing to negatively charged protoplasm, see *Biol. Bull.*, 1927, 52, 161 and 168.

Dr. G. S. Adair (*Cambridge*) said: The theory that the increase in the effective osmotic pressure of the plasma is partly due to the restraint by the capillary of the so-called diffusible calcium is of considerable interest. This osmotic effect should be partly determined by the nature of the membrane, since the rates of diffusion of solvent and solute affect the pressure with membranes that are not ideal, and partly by the effects of the protein on the osmotic coefficient of the calcium ions and on the Donnan distribution ratio.

Dr. W. Wilbrandt (*Bern*) said: Professor Krogh has pointed out that an exchange with tissue cells may play a rôle in the experiments reported. It seems to me, that the peculiar behaviour of potassium is a definite proof that this must be so. Potassium is more diffusible than sodium. The relative rise of its concentration should, therefore, be lower than that of sodium, if the results were really due only to incomplete diffusion exchange across the capillary wall. Since, in the experiments, the relative rise of potassium is in some cases as high as that of protein, exchanges with tissue cells, most probably muscle fibres, must come into play. The question may be raised, how it is possible at all to distinguish between such exchanges and the mechanism suggested by Professor Keys.

Dr. J. H. Schulman (*Cambridge*) said: Among the possible forces present in membranes which may serve for the transport of material along the membranes (*e.g.*, electrical and osmotic as suggested by T. Teorell), there may be surface forces: The electrical forces in membranes based on diffusion or diphasic potentials are not likely to be very large owing to the high salt concentration, which will diminish the potentials. Any mechanism capable of continuously modifying and subsequently reforming surface films should be capable of employing surface forces for transport of material (Van der Waals, polar or interchange forces, *e.g.*, circulation of taurocholic acid in connection with fat absorption through gut; protoplasmic streaming in plant cells).

Professor Ancel Keys (*Rochester, Minn.*), in reply, said: Though Krogh's definition of a membrane is an excellent one, I should like to suggest certain modifications to give the definition a more general character. I take a membrane to be a structure or a boundary phase, with main extension in two dimensions only, which will restrict or alter the free movement of molecules or particles without the expenditure of energy. Active or dynamic processes may be superimposed upon this simple membrane function and if these are present they must be differentiated sharply from the passive exchanges.

Definition of the type of system.—It is essential at the outset to decide the kind of system which is under consideration. I suggest that there are three main types, each of which will require a different theoretical approach:

(1) *Equilibrium systems.*—Here the classical procedures of thermodynamics and kinetics apply without alteration. It is doubtful, however, whether true equilibrium conditions are ever attained in living tissues except in special instances in resting organisms.

(2) *Steady-state systems.*—In resting organs or organs working at a constant rate steady states must occur frequently or even generally. A. V. Hill has pointed out the fundamental difference between steady state and equilibrium systems. The theoretical methods of analysing such steady-state systems must be greatly advanced before it will be possible to make satisfactory quantitative explanations of many exchanges across membranes in living organisms.

(3) *Non-equilibrium, non-steady-state systems.*—I believe the great majority of exchanges across membranes in active animals fall into this last category. Theoretical methods of dealing with such systems are practically non-existent as yet. It would seem possible only to state that the greater the divergence from equilibrium, the greater will be the force tending to establish equilibrium and, further, at no time will the passive

exchanges in such non-equilibrium, non-steady-state systems tend to increase the free energy of the system. At present such systems must be studied very largely by purely empirical methods.

Definition of the character of the exchanges across the membrane.—As suggested before, the exchanges across a membrane may be (1) passive, *i.e.*, involving no expenditure of energy, (2) active, *i.e.*, requiring the expenditure of energy and the performance of thermodynamic work, or (3) mixed, *i.e.*, passive exchanges altered or even reversed by the performance of thermodynamic work.

In any given case which is being studied it must be decided, as soon as possible, which type of exchange is involved. I believe that in the great majority of natural membranes it will be found that the exchanges are very largely passive, but, since most animal membranes are living, the metabolism of the membrane itself may contribute a small "active" component to the system.

In many cases it should not be difficult to decide the *general* character of the exchanges from the standpoint of energetics. It may, however, be much more difficult to make such decisions with regard to individual substances, particularly those which are normally involved in cellular metabolism, such as oxygen, carbon dioxide, urea, etc.

The points discussed here should be obvious: I feel constrained to mention them solely for the reason that it is abundantly clear they are often, or even usually, disregarded in discussing exchanges across membranes in living systems.

In reply to the question raised by Dr. Wilbrandt, I see no means at present to differentiate between the different types of exchanges when potassium is concerned. The question with potassium is very different from that with protein, calcium, and sodium. I think it highly likely that incomplete diffusion exchange also plays a part with potassium, but the high concentration of potassium in the tissue cells and the peculiar behaviour of potassium clearly indicate that, as Dr. Wilbrandt suggests, the analysis of the potassium exchanges must await other methods of attack.

METHODS OF MEASURING SURFACE FORCES OF LIVING CELLS.

BY E. NEWTON HARVEY.

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Naked cells only will be considered, cells whose surface is obviously liquid in behaviour, *i.e.*, is readily distorted and reconstitutes itself when broken without leaving frayed edges. Examples of such cells are *Amoeba*, leucocytes and marine eggs, which can be readily fragmented by shaking or centrifuging. Whether a plastic pellicle is present or not a determination of the sum of its surface and elastic tensions and its behaviour on stretching will give valuable information on its character and the magnitude of surface forces to be reckoned with in the living cell.

It is obvious that the classical methods of determining surface tension cannot be used with cells, but several independent methods available all show that: (1) the tension, *i.e.*, the sum of surface and elastic tensions is low, less than 1 dyne/cm.; (2) the surface has elastic properties.

The Centrifuge Method.—This assumes that a spherical cell behaves like a fluid droplet and becomes unstable when drawn into a cylinder of the same volume whose length is π times its diameter, breaking into two or more spheres. It is applicable to egg cells containing oil

globules (lighter than the cell fluid) and yolk granules (heavier than the cell fluid). Under the influence of centrifugal force the oil and yolk separate and exert stretching forces that pull the cell into two almost equal spheres.¹ At the moment of instability we may equate these forces to the tension (T) around the circumference of the elongated cylinder, thus:—

$$\pi DT = Cg[V_H(\rho_H - \rho_M) + V_L(\rho_M - \rho_L)],$$

where D = diameter of cylinder, C = centrifugal force in times gravity, $g = 980$, V_H = volume of heavy half, ρ_H = density of heavy half, ρ_M = density of medium, V_L = volume of light half, and ρ_L = density of light half.

The whole process of separation into two half cells can be watched (or photographed) in the centrifuge-microscope,² and the centrifugal force that is just sufficient to separate the two halves determined. Volumes and densities are easily measured. Results for the unfertilised eggs of a sea urchin, *Arbacia punctulata*, range around 0.2 dynes/cm. depending on the individual from which eggs are obtained and the time they remain standing in sea-water, for the tension increases with time. The surface of such an unstable cylinder would be about 25 per cent. greater than the surface of the original sphere, so that the value 0.2 dyne/cm. represents a 25 per cent. increase of the surface.

A modification of this method can be applied to cells into which oil drops have been injected. In this case the oil drop is pulled out by centrifugal force and the figure becomes unstable when a neck of protoplasm forms equal to the diameter of the oil drop. We equate the buoyant force of the oil when centrifuged to the tension around the circumference of the neck of protoplasm when the oil drop pulls away:—

$$\pi DT = Cg[V_O(\rho_M - \rho_O)].$$

When D = diameter of neck, V_O = volume of oil drop, ρ_O = density of oil, ρ_M = density of medium surrounding cell.

Values obtained by this method for *Amoeba dubia*³ are 1 to 3 dynes/cm.; for a slime-mould, *Physarum polycephalum*,⁴ around 0.45 dyne/cm., and for rabbit macrophages 2 dynes/cm.; frog leucocytes⁵ 1.3 dynes/cm.

Compression Method.—If it were possible to insert a micromanometer into a cell and measure the internal pressure (P), the relation $P = 2T/r$ would give a simple method of determining the tension (T) of a spherical cell of radius, r . Technical difficulties prevent its use, and in addition, the pressure would be measured in fractions of a millimetre of water. By the use of the general equation,

$$F/A = P = T(1/r_1 + 1/r_2),$$

and by measuring the force (F) necessary to flatten a cell a given amount, Cole⁶ has not only determined the tension of the unflattened egg, but obtained values for the increase in tension as the surface area increased on flattening. The eggs are flattened by a microbeam of gold, 6μ thick and 180μ wide, pressing on the top of the egg, and then photographed. The two radii of curvature (r_1 , r_2) can be measured from the photographs

¹ E. N. Harvey, *Biol. Bull.*, 1931, 61, 273.

² E. N. Harvey, *J. Franklin Inst.*, 1932, 214, 1.

³ E. N. Harvey and D. A. Marsland, *J. Cell. and Comp. Physiol.*, 1932, 2, 75.

⁴ D. Vexler, *Proc. Soc. Exp. Biol. and Med.*, 1935, 32, 1539.

⁵ H. Shapiro and E. N. Harvey, *J. Cell and Comp. Physiol.*, 1936, 8, 21.

⁶ K. S. Cole, *J. Cell. and Comp. Physiol.*, 1932, 1, 1.

and the pressure (P) calculated from F/A , where A is the area of the egg flattened by contact with the beam surface. The beam, held in such a manner that it always remains parallel to the plane of compression, is calibrated by hanging microweights on one end and noting its deflection by light reflected from the beam to a scale. The forces to be measured are of the order of 10^{-6} grams, 2 micrograms giving a compression of 25μ .

Results on the unfertilised egg of the sea urchin, *Arbacia punctulata*, 74μ in diameter, give a tension of 0.135 dyne/cm. when compressed 25μ , and lower values for less compression. Extrapolation of the tension-compression curve, which is slightly convex to the compression axis, to zero compression, gives a value of 0.08 dynes/cm. for the uncompressed egg. The evidence for elasticity of the surface is clear and conclusive. The fertilised egg of *Arbacia*⁷ without fertilisation membranes behaves as the unfertilised, and gives the same low values for surface forces until shortly before first cleavage but the fertilised eggs with fertilisation membranes behave as if the membrane were decidedly rigid and the values have no significance.

Kinetic Method.—Just before the completion of first cleavage of an *Arbacia* egg the two blastomeres are connected by a small stalk. If one blastomere is punctured, the remaining one will discharge its contents through the stalk due to an excess internal pressure from the tension at the surface. From moving pictures the rate of discharge can be determined by measuring the decrease in volume of the blastomere. It follows a law which would indicate elastic forces at the surface. Assuming Poisseuille's Law and using a measured value for viscosity of the egg fluid at this stage of development, Sichel and Burton⁸ calculated the excess internal pressure to be 62 dynes/cm.² and the tension 0.09 dynes/cm., agreeing well with the Harvey¹ and Cole⁶ figures for the same egg.

Sessile Drop Method.—The various equations relating the form of a flattened drop resting on a plane to the tension at its surface have been summarised and discussed by Dorsey.⁹ In general, the relation

$$T = g(d-d')r^2F$$

holds. T is the tension; g the force of gravity, $d-d'$, the difference in density between drop and medium; r the radius of greatest flattening, and F a function containing f , a term representing the flattening of the drop. Shapiro¹⁰ has given a table relating F and f for different degrees of flattening. These equations strictly apply only where pure surface tension is involved, i.e., only where the tension is independent of the extension of the surface. It is easy to calculate that most marine eggs are far too small to flatten appreciably under the influence of gravity even though their surface tension is assumed¹¹ to be 0.2 dynes/cm.

The egg of the mollusc, *Busycon canaliculatum*, 1 mm. in diameter, does flatten under the influence of gravity and gives a tension of 0.5 dynes/cm., while the egg of the salamander, *Triturus viridescens*, 1.5 mm. in diameter, gives 0.1 dyne/cm. The protecting membranes were, of course, first removed.¹² Both eggs cleave completely, so that any

⁷ K. S. Cole and Eva Michaelis, *J. Cell. and Comp. Physiol.*, 1932, 2, 121.

⁸ F. J. M. Sichel and A. C. Burton, *Biol. Bull.*, 1936, 71, 397.

⁹ W. E. Dorsey, *Sci. Papers Bur. Standards*, 1926, 21, 563; *J. Wash. Acad. Sci.*, 1928, 18, 505; *Bull. Nat. Res. Coun.*, 1929, No. 69, p. 56.

¹⁰ E. N. Harvey and H. Shapiro, *J. Cell. and Comp. Physiol.*, 1934, 5, 255.

¹¹ E. N. Harvey, *J. Cell. and Comp. Physiol.*, 1933, 4, 35.

¹² E. N. Harvey and G. Fankhauser, *J. Cell. and Comp. Physiol.*, 1933, 3, 463.

membrane at their surface must be non-rigid if not completely liquid in character. The sessile drop equations do not apply to cells with membranes.¹³

The most important application of the sessile drop equations is to small oil drops in living cells, made possible by the development of the centrifuge-microscope. Mackerel eggs contain a single droplet, 310μ in diameter, which flattens against the rigid cell membrane if the eggs are centrifuged. If photographed while revolving beautiful sharp profiles of flattened drops are obtained from which Harvey and Shapiro¹⁰ calculated the oil-protoplasm interfacial tension to average 0.6 dynes/cm. When the force was increased from 50 to 450 times gravity little change in the tension occurred showing that the surface did not possess marked elastic properties.

Danielli and Harvey¹⁴ studied the interfacial tension of egg oil extracted from mackerel eggs against various aqueous solutions, including egg extract, by means of the du Nouy tensimeter. It was found that low tensions (0.8 dynes/cm.) were obtained with oil in contact with egg extract but much higher ones with egg oil in contact with sea-water (7 dynes/cm.). Further analysis of the cause of the low tension pointed to a globulin-like protein as the surface active substance. We can thus picture the oil drop surface as made up of oriented oil molecules, the polar groups toward the water phase, covered with an adsorbed monolayer of hydrated protein molecules. Since the tension at the surface of cells is correspondingly low, perhaps the same picture can be formed of the cell surface, a thin oil film with adsorbed protein on either side, a thesis which has many observations in its favour.

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GENERAL DISCUSSION.

Mr. O. Gatty (Cambridge) said: The rôle of protein in the cell membrane is raised in the last paragraph of this paper and also in several later papers especially that by Professor Ponder.¹ The effect of tannic acid on the potential of frog skin suggests that the electrically active surfaces of frog skin have little exposed protein. Phenolic hydroxyl groups are supposed to associate with peptide linkages so it is interesting to note the further result that $M/200$ picrate added to Ringer at p_H 8 on both sides of frog skin depresses the potential but has little effect on skin resistance. The effect on the resistance supports the tentative conclusions from the tannic acid results, since the skin can hardly be supposed to have many protein pores of such a size that blocking with picrate ion has no appreciable effect on skin resistance. The effect of picrate on the potential may be due to its greater penetrating power and to its affecting metabolic or other processes inside the cell. Can it be that the protein occurs in appreciable areas only on the interior of the cell surface?

I would like to express a hope that the methods developed by Professor Newton Harvey will be used to determine the surface adsorption of electrolytes, drugs, and other substances on cell surfaces by use of Gibbs' adsorption equation. The importance of ionic adsorption on frog skin potential is discussed in another paper.

Professor E. Newton Harvey's reply, if received before going to press, will be inserted at the end of this number.

¹³ E. N. Harvey, *J. Cell. and Comp. Physiol.*, 1936, 8, 251.

¹⁴ J. F. Danielli and E. N. Harvey, *J. Cell. and Comp. Physiol.*, 1935, 5, 483.

¹ Page 947.

THE PHYSICAL STRUCTURE OF THE RED CELL MEMBRANE, WITH SPECIAL REFERENCE TO ITS SHAPE.

BY ERIC PONDER.

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1. The Discoidal Form of the Mammalian Erythrocyte.

When in serum or plasma, the shape of the mammalian red cell is that of a biconcave disc, the dimensions of which vary slightly from cell to cell, and considerably from one species of animal to another. The only way of defining the shape with any degree of exactness is to photograph cells on edge, and make measurements from the plates.^{1c} So far, the only cells whose shape has been satisfactorily defined are those of man, the rabbit, and the sheep. Except for an empirical equation which gives the shape of the cell in terms of a Fourier series,^{1a} no mathematical expression for the shape has been found, although it has been pointed out that the surface approximates to one of equi-velocity potential to a ring, so that gas molecules starting from the cell surface at any one time all converge on this ring at the same moment, a condition suited to the even diffusion of gases throughout the cell volume.^{1a}

For our purpose, the explanations which have been put forward for the shape of the mammalian red cell fall into two categories, those which postulate an *internal* structure, and those which look upon the *surface* of the cell as the seat of the forces which maintain the special form. The theory of Rollett, who thought of the cell as having a dense internal stroma, and a number of modifications of the original Rollett theory,² fall into the first category, while theories of the second category are all variants of the hypothesis put forward in 1882 by Norris,³ who, like several others,⁴ was impressed with the similarity between the shape of the red cell and that of the "myelin forms" which are assumed by droplets of lecithin in water. The latter are described as circular discs, dumb-bell in cross-section, and about 5μ to 10μ in diameter. They are apparently produced by physical forces at the interfaces between the droplets and the surrounding fluid, and Norris suggested that the biconcave form of the mammalian erythrocyte is brought about in a similar way. Thus, as Gough puts it, there are two sets of forces operating, the first of which tends to produce contraction of the surface and the spherical form, while the second tends to bring about expansion of the surface and a very flattened form; balanced against each other, the two sets of forces maintain the discoidal form.

¹ (a) Ponder, E., *J. gen. physiol.*, 1926, 9, 625. (b) *J. exp. Biol.*, 1929, 6, 387. (c) *Quart. J. exp. Physiol.*, 1930, 20, 29. (d) *J. gen. Physiol.*, 1933, 17, 617. (e) *Quart. J. exp. Physiol.*, 1933, 23, 287. (f) *J. exp. Biol.*, 1936, 13, 298. (g) *Protoplasma: In Press*, 1936. (h) *Proc. Soc. exp. Biol. and Med.*, 1936, 33, 630. (i) *J. exp. Biol.: In Press*, 1937.

² E.g., that of Emrys-Roberts, E., *J. Path. and Bact.*, 1920, 23, 357.

³ Norris, R., *The physiology and pathology of the blood*, 1882, London, Smith Elder.

⁴ (a) E.g., Rice, J., *Phil. Mag.*, (6), 1914, 28, 664. (b) Gough, A., *Biochem. J.*, 1924, 18, 202.

Some idea of the forces required may be obtained by drawing a cross-section of the red cell, finding the two principal radii of curvature, ρ_1 and ρ_2 , at each point, and computing the pressure P which would have to be applied to keep a homogeneous cell membrane, with tension T , in hydrostatic equilibrium:—

$$P = T(1/\rho_1 + 1/\rho_2).$$

It appears that we have to have a pressure directed outwards over the equatorial regions of the cell, and a smaller pressure directed inwards over the biconcavities, if we are to account for the shape in this way.^{1a} The idea that such pressures really exist, is, of course, untenable, but the "outward pressure over the equatorial regions" is the same as Gough's "expansive force." This might arise in one of two ways:—

(1) The molecules in the cell interior, and particularly the hæmoglobin molecules, might repel each other more in one direction than in another, and this is precisely Gough's modification of Norris' theory. Teitel-Bernard⁵ has put forward a hypothesis very similar to Gough's. The hypothesis is not impossible in itself, although it is disproved by the fact that hæmoglobin-free ghosts obtained after "reversal" of hypotonic hæmolysis are discoidal.^{1b} We can modify it once again by suggesting that the "stromatin" micelles, which, according to Boehm, are both anisodiametric and distributed throughout the cell interior, repel each other more in one direction than another.

(2) Similar repulsive forces may occur between the molecules in the cell envelope, and these will oppose the surface tension forces at the interfaces on either side, which tend to produce the smallest surface for the enclosed volume. Equilibrium will be reached when the surface forces are balanced by the expansive forces, so that at equilibrium the free energy will be at a minimum, although the surface may not be the minimum for the enclosed volume. It is not difficult to see how such mutual repulsion between molecules in the envelope might arise, for hydrocarbons with a polar group directed towards the water (COOH groups, for instance, as in lecithin) would tend to be mutually repulsive. Under such circumstances, however, the tensions along the membrane would have to vary from place to place (if the pressures are to be the same), and so Norris' theory really demands that the (molecular) structure of the membrane shall not be homogeneous. This is tantamount to saying that the membrane has a "liquid crystal" structure.

The first problem, accordingly, is to decide whether the biconcave form of the red cell is due to forces operating in its interior or to forces in the neighbourhood of its surface, and it would be easier to do so if we knew more about its structure. Rollett's theory demands an internal stroma: does the red cell have one? Microscopical observation, either with direct illumination, with the dark field, or with ultra-violet light, tells us little one way or the other; no structure can be seen, but both the colour and the high refractive index of the hæmoglobin would tend to make a fine network invisible, even if it were there. No structure is visible even in the hæmolysed ghosts, but one can quite well have something of the nature of a "stroma" which looks homogeneous under the microscope. The evidence from microdissection studies is equally inconclusive, for while the puncture of a red cell in NaCl may sometimes result in a jelly-like mass being left behind, a needle can be thrust through a cell in plasma, and moved to and fro in all directions without resist-

⁵ Teitel-Bernard, A., *Arch. roum. Path. exp. Microbiol.*, 1932, 2, 389.

ance after the cell has hæmolyzed.⁶ The jelly-like masses which can be teased to shreds⁷ may represent either gelated cytoplasm or remains of the cell wall, and Boehm has pointed out that the protein, "stromatin," contained in the red cell in a concentration of about 4 p.c., is capable of forming a remarkably rigid phase throughout the cell volume, because of its micellar structure. Turning next to the structure at the cell surface, we find a distinction between the cell "wall" or "envelope," and the cell "membrane," the former being at least thick enough to be visible ($> 0.2\mu$), while the thickness of the latter is regarded⁸ as being about 0.003μ ; the "envelope," according to this current view, is a supporting structure only one or two layers of which are specialised so as to be the seat of the permeability properties of the surface. We have no indication of how forces responsible for the shape of the cell might arise at such a surface, and in fact both Rollett's theory and Norris' theory demand a special kind of "structure," in a broad sense (a "stroma," or a special molecular orientation at the surface), and we have no direct evidence that the required structures exist. Let us see, however, what information can be gained from a study of the changes in shape which the erythrocyte can undergo.

2. Disc-Sphere Transformations.

Mammalian red cells in saline¹⁰ become perfectly spherical, without change in volume, if enclosed between a slide and a closely applied coverglass, and the same change occurs¹⁰ if lecithin is emulsified in the fluid surrounding the cells. There is a similar shape transformation in the case of red cells treated with various dyes of the fluorescein series,¹¹ and it has now become clear that all these shape changes are closely connected with the phenomenon of hæmolysis, which invariably follows the disc-sphere transformation after sufficient time, and which is invariably preceded by it. Each of the methods of producing the spherical form of the red cell has special points of interest connected with it, and I shall describe the principal ones *seriatim*.

(a) **The Spherical Form between Two Surfaces.**—The description of this phenomenon begins with the observation⁹ that the normally biconcave red cell becomes a perfect sphere in saline or sugar solutions, but not in media containing appreciable quantities of serum or plasma. Although the first description of the spherical form of the erythrocyte, Hamburger's observation was wrong in that he thought that the cells become spheres because of the nature of the medium in which they are immersed, and not until 1920 did Brinkman and van Dam¹⁰ correct the description by pointing out that red cells floating freely in saline are not spherical, but discoidal, and that the spherical form is only assumed when they come in contact with glass, as in a hæmocytometer chamber. In becoming spheres, the cells pass through an intermediate, crenated, "thorn-apple" form, and Brinkman and van Dam believed that the cause of the phenomenon is that the cells receive an electrostatic charge when they touch the floor of the chamber. They confirmed Hamburger's statement that the change from disc to sphere is prevented by serum or plasma, and thought that it is the cholesterol contained in serum and plasma which is responsible for the

⁶ Chambers, R., *Personal communication*, 1937.

⁷ Seifritz, W., *Protoplasma*, 1927, 1, 345.

⁸ Fricke, H., *J. gen. Physiol.*, 1925, 9, 137; Danielli, J. F., *J. gen. Physiol.*, 1935, 19, 19.

⁹ Hamburger, H. J., *Arch. ges. Physiol.*, 1895, 141, 230.

¹⁰ Brinkman, R., and van Dam, E., *Biochem. Z.*, 1920, 108, 52.

prevention. Gough⁴⁵ described the same phenomenon, but fell into Hamburger's original error, and in 1929 I repeated Brinkman and van Dam's experiments, only to find, however, that their description too was incomplete, and that the essential condition for the disc-sphere transformation is that the cells, in saline, should be enclosed between *two closely applied surfaces*, such as slide and coverglass.¹¹

Mammalian red cells, suspended in 1 per cent. NaCl or any of the ordinary physiological salines, and examined in a hanging or uncovered drop, are discoidal, although often crenated; at all events, they are not spherical. If the same cells, however, are covered with a coverglass, and if the drop of fluid is sufficiently small to allow the coverglass to make close contact with the slide, all the cells become perfectly smooth spheres of the same volume as that of the original discs. If the two glass surfaces are close together, the transformation from disc to sphere takes place very rapidly, but by constructing a wedge-shaped chamber, about 1 mm. deep at one end and about 40μ at the other, it can be seen that the cells are discoidal at the deep end and spherical at the narrow end, the cells in an intermediate position being "thorn-apple" forms. This "thorn-apple" form always appears as an intermediate stage in disc-sphere transformations, the sphere being the final result of a progressive process of crenation.

By running a little serum or plasma under the coverslip, the spheres can be re-converted into biconcave discs, which differ from normal discs, however, in being unusually sticky. Under dark-ground illumination their surfaces frequently appear mottled. The discoidal form is usually maintained if the dilution of the serum is less than about 1 in 25, and the substances responsible for the reversal seems to be a serum protein, and not cholesterol.

No satisfactory explanation has been advanced for this shape transformation. There appear to be three necessary conditions, (a) that the cells shall be in a plasma-free medium, (b) that they shall be enclosed between two closely applied surfaces, and (c) that the surfaces shall be wetted by the suspension medium. The phenomenon is certainly not due to the cells receiving electrostatic charges from the glass, nor to alkali dissolving from the glass,¹¹ nor to the pressure exerted between two closely applied surfaces separated by a liquid film. So far as the nature of the forces maintaining the discoidal shape of the cell is concerned, the only immediate point of interest is that the reversal of the transformation is brought about by the serum proteins. These substances are not likely to penetrate the cell membrane, and so their effect is probably upon surface components.

(b) **The Spherical Form in Lecithin-Treated Plasma.**—A similar disc-sphere transformation occurs in serum, plasma, or saline to which small quantities of lecithin have been added, and again the normally discoidal cells become perfect spheres without change in volume. To obtain the spherical form, one separates plasma from the blood, and emulsifies about 5 mg. of lecithin for each c.c. of plasma. If this lecithin-treated plasma is mixed in about equal proportions with whole blood, the cells first crenate and assume the "thorn-apple" form; the crenations then become progressively finer, and ultimately disappear, leaving perfect spheres. These remain unchanged for a period which depends on the amount of lecithin added, but finally undergo hæmolysis. There is some evidence that the quantity of lecithin which has to be added in order to effect the transformation varies in the case of the cells of different animals, but quantitative work still requires to be done on the subject; the difficulty is that the present method of introducing the lipid into the suspension medium (mechanical emulsification) is unsatisfactory, and results in varying quantities being emulsified.

The disc-sphere transformation can be reversed by washing the cells in untreated serum, plasma, or saline. When the reversal occurs, all the

¹¹ Waller, W. W., *J. Physiol.*, 1930, **70**, 42P.

changes are seen in the reverse order; first fine crenations appear, these become coarser, and finally the cells become discoidal, often with irregular crenations. The disc-sphere transformation and its reversal can be repeated several times under favourable circumstances, but each repetition results in more and more hæmolysis.

(c) **The Spherical Form Produced by Photodynamic Dyes.**—Mammalian red cells in NaCl, or in any of the common saline solutions, rapidly become spherical if small quantities of fluorescein, eosin, erythrosin, or rose bengal, are added. If smaller quantities are added, the cells assume the "thorn-apple" form; still smaller quantities leave the shape unchanged, and the sequence of shape changes which ends with the spherical form is the same as in the case of the disc-sphere transformation between slide and coverglass or in lecithin-treated media. The most careful measurement shows that the change of shape is unaccompanied by a change in volume.

The quantity of dye required to bring about the shape change varies in the case of the four dyes of the fluorescein series. Using 0.2 c.c. of a 4 per cent. suspension of washed rabbit red cells, and 1 c.c. of dye, one requires a concentration of about $M/10^5$ in the case of rose bengal, $M/10^4$ in the case of erythrosin, $M/10^3$ in the case of eosin, and $M/10^2$ in the case of fluorescein: these concentrations are about ten times less than are required to produce lysis in the dark, but about the same as bring about lysis in bright light.¹² Taking the case of rose bengal and the rabbit red cell, where the area of the spherical form is about $80\mu^2$ and where a rose bengal concentration of about $5M/10^6$ is needed to effect the shape change, we find that the amount of dye present in the system in which the disc-sphere transformation occurs is just about enough to cover the cell surfaces with a monomolecular layer. The change of shape, in this case at least, is presumably brought about as a result of an effect on a surface component.

The spherical forms in systems containing the photodynamic dyes can be immediately re-converted into discs by the addition of serum or plasma in small amounts (0.002 c.c. added to a system containing 0.2 c.c. 4 per cent. cells and $M/10^5$ rose bengal). The active component of the serum seems to be a protein, and the re-formed discs show the same stickiness, slight crenation, and mottling of the surface as are found when spheres, produced between slide and coverglass, are re-converted into discs by the addition of serum or plasma.

(d) **Spherical Forms Produced by Lysins.**—It is now recognised that all forms of hæmolysis are preceded by a disc-sphere transformation, this sometimes occurring almost immediately before hæmolysis, and sometimes a considerable time before. What happens appears to be that at a certain stage of the action of the lysin on the cell membrane, a "shape component" gives way, and the cell, quite suddenly, becomes spherical; after further action a "permeability component" breaks down, and the cell becomes permeable to hæmoglobin, and hæmolyses. This sequence of events can be observed in systems containing saponin or other glucosides, the bile salts or the soaps, complement and amboceptor, colloidal silicic acid and complement, brilliant green and serum, or, in fact, any lysin, and a similar shape change precedes lysis in systems subjected to heat or radiations. Even in the case of hypotonic hæmolysis there is evidence of a breakdown of a "shape component" preceding that of the "permeability component," for the spherical form which the cell assumes just before lysis is not merely the result of continuous swelling and deformation up to the point where the original surface encloses a sphere, but is assumed suddenly, the cell changing from a swollen or cup-shaped body into a perfect sphere in much the same way as it changes into a sphere under the action of saponin.¹³

This being so, it will be apparent that the disc-sphere transformations which occurs in lecithin-treated media or in systems containing the dyes of the fluorescein series are merely special cases of the shape transformation

¹² Blum, H. F., *Cold Spring Harbor Symp. Quant. Biol.*, 1935, 3, 318.

which occurs with lysins in general, although they are distinguished by the fact that the shape change and the ensuing lysis are separated by a long time interval, or, alternatively, that the shape change and the permeability change occur in concentrations of different orders. Although it is true that the phenomena are far from being explained, there are certain conclusions which we can draw from the evidence, if we take it as a whole.

(1) Although the loss of the discoidal shape of the cell and the loss of its semi-permeability are two stages in one lytic process, the former always preceding the latter, the structures, or forces, which are responsible for the shape can be destroyed, or overcome, without any apparent change in the permeability properties. Thus the volume of the spherical form is the same as that of the discoidal form from which it is derived, irrespective of whether the suspension medium is isotonic, hypotonic, or hypertonic,^{12,7} and the osmotic properties of the spheres seem to be substantially the same as those of the discs. There is no appreciable change¹³ in the resistance, capacity per unit area of cell surface, or frequency dependence of the capacity, when the disc-sphere transformation occurs, nor is there appreciable change in the ζ -potential when the transformation takes place in saponin solutions.¹⁴ It seems that the breakdown of the "shape component" modifies the permeability and electrical properties of the cell remarkably little.

(2) The substances which produce the spherical form most readily (*e.g.*, lecithin and the photodynamic dyes) are not, in general, substances which would be expected to penetrate into the cell interior and affect either structures within the cell (*cf.* Rollett's theory), or the molecular state of hæmoglobin (*cf.* Gough's and Teitel-Bernard's hypotheses). In the case of rose bengal and hæmatoporphyrin, the changes in form are brought about when there are barely enough molecules to cover the cell surface, let alone penetrate and affect internal structures. Further, the change from disc to sphere occurs immediately on the addition of serum to rose bengal systems, and the serum proteins, which seem to be responsible for the reversal, are scarcely substances likely to enter the cell interior. All the evidence, in fact, points to changes in shape being due to the action of substances at the red cell surface.

(3) It is interesting that many of the properties of the red cell membrane depend on whether the cells are bathed with serum or plasma or with saline media. Thus the disc-sphere transformation which occurs between slide and coverglass and the transformation which follows the addition of photodynamic dyes do not take place in the presence of serum or plasma, which revert into discs any spheres which may be present. Again, the irregular crenation which is often seen in the cells of saline suspensions does not occur either as frequently or as markedly when serum or plasma is the surrounding medium, and the extent to which red cells can swell, and their membranes stretch, without losing pigment into hypotonic solutions, is greater in hypotonic serum or plasma than in hypotonic saline. There is some evidence, too, that the permeability of the cell membrane is not the same when it is stretched in hypotonic plasma and in hypotonic saline respectively.¹⁵ All these observations point to the presence of some plasma constituent as being necessary for the maintenance of the normal properties of the membrane.

3. The Ultrastructure of the Red Cell Membrane.

The study of the disc-sphere transformations and of the conditions under which they occur leads us to the conclusion that the changes of shape are probably due to the action of substances at the surfaces of the

¹² Curtis, H. J., *J. gen. Physiol.*, 1935, 19, 929.

¹⁴ Abramson, H., *Electrokinetic phenomena*, Chemical Catalog Co., New York.

1924.

¹⁵ Ponder, E., and Robinson, E. J., *J. Physiol.*, 1934, 83, 34.

cells, and so it is probable that the component which maintains the normal shape is a surface component. This brings us back to Norris' theory, which demands something of a "liquid crystal" structure at the cell surface, and it is interesting to observe that other facts, such as the permeability properties¹⁶ and the action of lysins¹⁷ suggest that the envelope should be regarded as a protein-lipoid complex. By X-ray analysis and by the methods of polarisation optics, the protein-lipoid complexes which exist in other cell membranes, such as in the axon sheath, have been shown to exhibit micellar orientation,¹⁷ and it is interesting to see if similar evidence of an ultrastructure can be found in the case of the red cell membrane. The only material which can be satisfactorily used are ghosts of cells which have been hæmolyzed by freezing and thawing, for the presence of any appreciable amount of hæmoglobin interferes with the optical analysis. A conventional polarisation microscope is used in conjunction with a very intense source of light and a $\lambda/20$ mica plate compensator, by which means the weak polarisation crosses are rendered more readily visible.

The optical properties of the red cell envelope are very like those of the axon sheath, and, as in the latter, are referable to two components, lipoids and proteins, the former showing a positive birefringence, and the latter a negative form birefringence. Since the sign of birefringence of these two components is opposed, their presence has to be demonstrated by varying the experimental conditions so that one or the other will predominate. Thus in isotonic NaCl, the birefringence is very low and negative, because the negative form birefringence of the proteins is offset by the positive micellar double refraction of the lipoids, although the latter contributes slightly less to the sum than the former. But the lipid birefringence can be increased by reducing that due to the proteins, e.g., by adding glycerine to increase the refractive index of the medium, while the protein contribution can be increased by adding lipid solvents, or even water, which bring about a partial destruction of the lipid orientation. In the former case, the weak negative birefringence is replaced by strong positive crosses characteristic of oriented lipid, while in the latter case the invariable result is the production of definite negative crosses referable to the negative form birefringence of the proteins.¹⁸

From these optical properties, the structure of the envelope of the ghost may be interpreted as consisting of layers of protein particles or lamellæ, with long axes oriented tangentially, and interspersed lipid micelles with optical axes oriented radially. Roughly speaking, the structure is not unlike that suggested by Danielli and Davson¹⁶ to account for the permeability properties of the cell, except that their protein and lipid layers are repeated again and again. This view as to the structure of the envelope is certainly very different from the usual one, but it must be remembered that the idea that the permeability properties of the cell are determined by a bimolecular layer of lipid, some 0.003μ thick, is based solely on an interpretation of impedance measurements. A more detailed analysis of the impedance data leads to the conclusion that the layer in which the permeability properties are resident may be many times thicker than has hitherto been thought,¹⁹

¹⁶ Danielli, H. F., and Davson, H., *J. cell. and comp. Physiol.*, 1934-35, **5**, 495.

¹⁷ Schmitt, F. O., *Symp. Quant. Biol.*, 1936, **4**, 7.

¹⁸ Schmitt, F. O., Bear, R. S., and Ponder, E., *J. cell and comp. Physiol.*, 1936, **9**, 89.

¹⁹ Fricke, H., *Personal Communication*, 1937, and see Fricke, H. and Curtis, H. J. J., *physical Chem. : In Press*.

and so the two lines of evidence do not really lead to divergent views. There is much greater difficulty in reconciling the existence of the ultra-structure with Gorter and Grendel's results,²⁰ which go to show that the lipoids extractable from the red cell are only sufficient to form a bi-molecular layer at the surface. Either Gorter and Grendel's indirect method underestimates the area which can be covered by the cell lipoids when distributed in a complex such as the red cell envelope, or some of the substances which give the positive birefringence which has been referred to the presence of lipoids are substances other than extractable lipoids; at all events, there is an incompatibility which has to be faced.

It is scarcely necessary to point out that the mere demonstration of an ultrastructure in the red cell membrane does not explain the peculiar shape or establish Norris' theory. All that it does is to replace the idea of the cell envelope as a liquid film containing a bimolecular layer of lipid molecules by an oriented protein-lipoid structure, and it is only a possibility that the forces which arise between the oriented molecules are such as to bring about the biconcave discoidal form.

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GENERAL DISCUSSION.

Professor E. Gorter (Leiden) said: I should like to draw particular attention to the following special points in Professor Ponder's paper. (1) In treating the transformation of red blood cells by the action of photodynamic dyes, he says, "we find that the amount of dye present in the system in which the disc-sphere transformation occurs is just about enough to cover the cell surfaces with a monomolecular layer." Then as we have not ourselves studied photodynamic dyes, I must quote what he says about hæmolysis: "It is now recognised that all forms of hæmolysis are preceded by a disc-sphere transformation." This is in very good agreement with our results on hæmolysis. We have, already long ago been able to show that in red blood cells there is present as much lipid as would cover two surfaces of the red cells. Now the amount of saponin which is just sufficient to produce complete hæmolysis, is just enough to cover the cell surface with a monomolecular layer. This can easily be shown if you use a good spreading saponin such as parillin or digitonin.

Mr. O. Gatty (Cambridge) said: Is it certain that oxygen lack has no effect on the sphere disc transformation or else excess of CO_2 or low p_{H} ? The necessity for the close proximity of two glass surfaces suggests that the cells have to be confined to a small volume in order to allow certain changes of concentration to take place. Some workers have measured the potential of a wire connecting two platinum electrodes and found it to vary as the distance between the electrodes is greatly reduced. Gatty and Spooner account qualitatively for their observations in terms of local action currents arising as the oxygen confined between the platinum electrodes gets used up. Erythrocytes may have a low Q_{O_2} but might show glycolytic activity. Is it a coincidence that many photodynamic dyes are Pasteur effect inhibitors?

Dr. J. H. Schulman (Cambridge) said: Professor Gorter's point that a unimolecular layer of saponin is required to be adsorbed on to the red cell membrane before hæmolysis occurs, is supported by experiments done on the hæmolysis of red cells with fatty acids. Apparently a unimolecular layer is formed on the red cell, sensitising the cell, hæmolysis

²⁰ Gorter, E., and Grendel, F., *J. exp. Med.*, 1925, 41, 439.

only taking place when further soap is added. A theory that sensitisation is due to the acid buffering of the protein of the red cell membrane, thus inactivating the "penetrating" properties of the soap (first adsorbed soap) has already been suggested.¹

Professor E. Ponder (*New York*), in reply (*communicated*): I am doubtful as to the significance to be placed on Professor Gorter's observation that the amount of saponin which is just sufficient to produce complete hæmolysis is just enough to cover the cell surface with a monomolecular layer. I obtained a similar result in 1930 for sodium oleate, although I was doubtful in that case, as I still am in the case of rose bengal, whether there are enough molecules to make the monolayer. When one takes the amount of lysin which produces complete hæmolysis, one must remember that a large proportion of this is combined with the hæmoglobin which leaves the cells which hæmolyse first; the result is that if the total amount can be spread in a monolayer which would just cover the cell surface, the surface of the cells in the system must have been covered with less than a monolayer, *i.e.*, in patches.

If we accept the idea that a monolayer must be formed, a difficulty arises in the case of substances such as erithrosine and eosin, etc., for the lytic concentrations of these dyes are respectively 10-fold and 100-fold that of rose bengal. Thus the quantity of dye in the system is far greater than would be needed to form a monolayer, and we would have to postulate an unstable monolayer which requires a definite concentration of dye to maintain it.

To my mind there are several objections to the idea that hæmolysis can be explained in terms of monolayer formations. The first I have mentioned: in many cases there are not enough molecules to go around, and in many other cases, the number of molecules contained in lytic concentrations are far greater than would be required to form a monolayer. The second objection is that substances such as rose bengal are not likely to form good monolayers because of their molecular shape. The third objection is that there is no change in zeta-potential when cells assume the spherical form just before lysis. The observations on zeta-potential, in fact, are more in accordance with some kind of "patch" theory.

I prefer to look at the process in a different way. The cell surface contains long protein chains and also oriented lypoid, and the action of a molecule such as that of rose bengal, with its large number of polar groups (tetraiodo-tetrachlor-triphenylmethane), would be to unite with the linkages in the protein side chains and so would have a solvating effect, and produce molecular disorientation. Erithrosine, eosin, and fluorescein, with decreasing polarity in that order, are decreasingly lytic, as one would expect. On this hypothesis, the kinetics of the hæmolytic process would be something like the kinetics of the conversion of β -keratin to α -keratin at increasing relative humidities, or the kinetics of the dyeing of wool. In both cases, the process follows a more or less exponential course, but theory would demand a falling velocity constant such as is found in studies on hæmolytic systems.²

In answer to Dr. Gatty, while changes in oxygen and CO_2 tension may well have an effect on the red cell shape (*e.g.*, in the sickling phenomena), I doubt if they have anything to do with the spherical form between slide and coverglass. If a dry coverglass is placed on a dry slide and a drop of the suspension is run between them, the cells become spherical within a fraction of a second after they pass between the two glass surfaces. I am still inclined to regard the phenomenon as due to an orienting effect of the glass surfaces on a liquid crystal structure at the red cell surface.

¹ Schulman and Rideal, *Proc. Roy. Soc. B*, 1937, 122.

² Ponder, *Biochem. J.*, 1935, 29, 1263.

A RELATION BETWEEN THE PERMEABILITY OF THE RED CELL AND ITS METABOLISM.

BY WALTER WILBRANDT.

Received 5th March, 1937.

It is known that the salt content of most cells of the human body differs widely from the composition of the environment, especially with respect to potassium. Thus these cells must all have gone through a stage of accumulation. For the human red cell, which, living in a medium rich in Na and poor in K, contains prevalingly or exclusively K, a change in permeability after this stage must be assumed, because it is known to be anion permeable. It has, however, been observed,¹ that under certain conditions the cell may loose this selective anion permeability, which leads to salt leakage. The present paper is to show, that a relation exists between the metabolism of the cell and the maintenance of this selective permeability.

The permeability of human erythrocytes was investigated by means of a photoelectric method, very similar to that described by Ørskov and Netter.²

It was first found, that, if a suspension of 1 c.c. human blood in 10 c.c. of 0.95 per cent. NaCl + N50 NaF (NaF suspension) is kept at 37° for a few hours, its time of osmotic hæmolysis in isotonic glycerol solution (an arbitrary degree of light transmission being chosen as test point) is lengthened considerably, as compared with a control suspension in 1 per cent. NaCl without NaF (NaCl suspension). Investigation of the question, whether this is due to a change in rate or in equilibrium, showed that the permeability for glycerol is not changed, or only slightly changed, while the equilibrium is shifted considerably.

The latter was shown in the following way. 1 c.c. each of the NaF suspension and of the NaCl suspension were added to a series of NaCl solutions of various concentrations from 0.0 to 1.0 per cent. (10 c.c. each) and the light transmission was measured, after equilibrium was established. The resulting curves of osmotic fragility showed two differences: (1) The curve of the NaF suspension is shifted to the side of lower concentrations, *i.e.* hæmolysis begins only at lower concentrations, for instance at 0.2 per cent. instead of 0.4 per cent. (2) Also at the higher concentrations, where no hæmolysis occurs, the light transmission of the NaF series is lower, due to a decrease in volume of the cells. The light transmission of blood suspensions depends not only on the number of cells, which are not hæmolysed, but also on their size; it is lower in higher salt concentrations, where the cell volume is smaller.

That the permeability for glycerol is not changed or only slightly changed, is shown by the following experiment. The light transmission of 1 c.c. NaF suspension and that of 1 c.c. NaCl suspension in 10 c.c. of 0.4 per cent. NaCl each are determined, after equilibrium is established. These two values of light transmission correspond to the same relative volume of the cells of the two suspensions, assuming the cells to act like osmometers. Then osmotic hæmolysis is brought about with 1 c.c. of

¹ Davson, *Biochem. J.*, 1934, 28, 680.

² H. Netter and S. L. Ørskov, *Arch. ges. Physiol.*, 1933, 231, 135.

each suspension in 10 c.c. of 0.2 per cent. NaCl + 0.3 *M* glycerol and the times to reach these relative volumes are measured for each suspension. These times are a measure of the permeability, independent of the differences in equilibrium. They differ only slightly for the two suspensions.

The shift of the osmotic resistance curve might be due to a change in the resistance of the membrane or to a decrease in amount of osmotically active substance in the cell. The decrease of cell volume shows that the latter is true. This loss of osmotically active substance must be due to salt leakage, the effect (loss of 50 per cent. in some experiments) being too great as to be explained otherwise. Chemical analysis has confirmed this assumption: the cells in the NaF suspension show a considerable loss of potassium.

NaF is a strong enzyme poison, which inhibits glycolysis in blood. The question arose, therefore, whether the NaF effect described above is

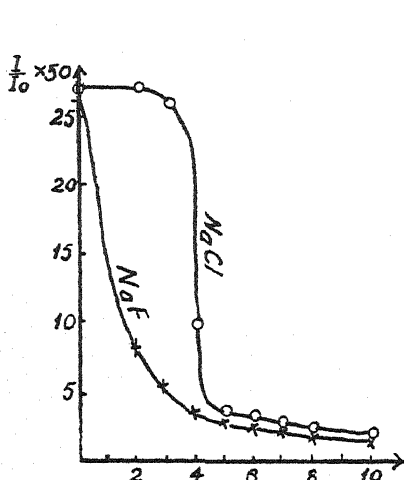


FIG. 1.—The change in osmotic fragility brought about by NaF after 11 hours at 37°. Ordinates: light transmission of the suspension as a measure of degree of hæmolysis.

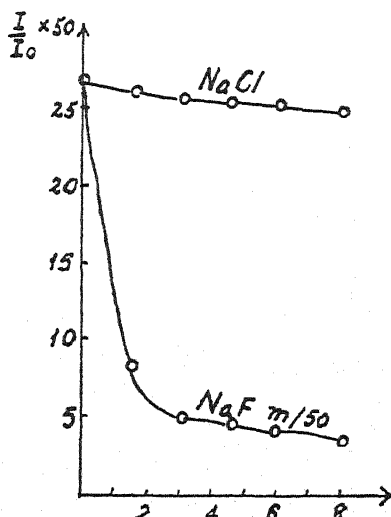


FIG. 2.—Time curve of the change in osmotic fragility. Ordinates: light transmission of a suspension in 0.25 per cent. NaCl, as a measure of the degree of hæmolysis in this concentration.

due to a change in metabolism of the cells. The following evidence, that this is so, has so far been collected.

Iodoacetate, which also inhibits glycolysis, acting, however, on different parts of the enzyme system, also produces the same effect as NaF. The lowest effective concentrations of both poisons are about the same in inhibiting glycolysis and shifting the osmotic resistance. The onset of the iodoacetate effect is about one to two hours later than that of the NaF effect. The same is known from their effects on glycolysis in muscle. Furthermore, Dische has shown,³ that the inhibiting effect of NaF on glycolysis is suppressed by pyruvate. Correspondingly the effect of NaF on the osmotic fragility of erythrocytes is diminished or completely suppressed after the addition of sodium pyruvate.

³ Z. Dische, *Encymologia*, 1936, 1, 288.

Fig. 1 shows the change in the curve of osmotic fragility of a NaF suspension. In order to investigate the time curve of this change, a NaF suspension was kept at 37° and samples were hæmolyzed from time to time in 0.2 per cent. NaCl, in which concentration hæmolysis is normally complete, after the treatment with NaF however incomplete. Fig. 2 shows the type of curve, that is thus obtained. Fig. 3 shows corresponding curves with iodoacetate in various concentrations. Fig. 4 shows the counteraction of pyruvate against NaF.

Mond⁴ has shown, that in alkaline reaction the anion permeability of ox red cells changes into cation permeability. The action of NaF and iodoacetate is not a p_H effect. All experiments were carried out in M/30 phosphate buffered solutions, whose volume was twenty times that of

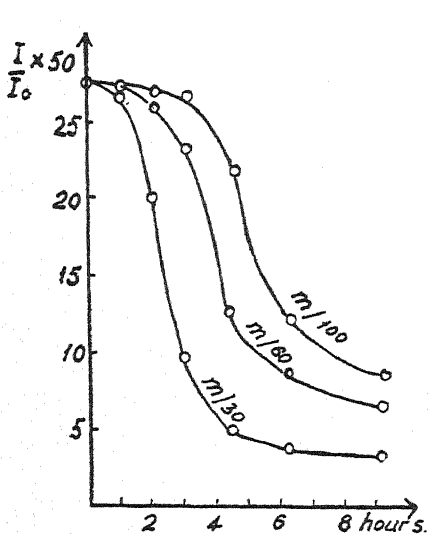


FIG. 3.—Time curve of the change in osmotic fragility brought about by iodoacetate. Ordinates: light transmission as a measure of the degree of hæmolysis of a suspension in 0.2 per cent. NaCl.

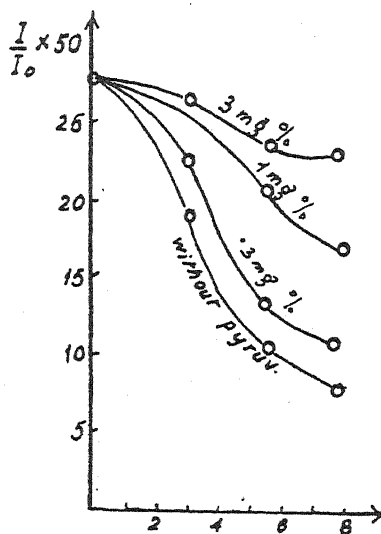


FIG. 4.—Inhibition of the change in osmotic fragility brought about by NaF N/50 by the addition of pyruvate in increasing concentrations. Ordinates: light transmission as a measure of the degree of hæmolysis in 0.2 per cent. NaCl.

the cells. The NaF effect occurs equally well at p_H 5.9, 6.8 and 7.6, that of iodoacetate is weakened at p_H 6.8 and suppressed at p_H 5.9.

There are some instances known, where the biological inhibitory effect of iodoacetate is compensated by addition of certain metabolites, whose formation is inhibited by iodoacetate, for instance lactic acid, glycerophosphate and others. This has, for instance, been shown in the secretory activity of the liver in Höber's laboratory⁵ and in tubular secretion of phenol red in tissue cultures of the chicken mesonephros by Beck and Chambers.⁶ We sought to ascertain whether the above described effect could be similarly suppressed by the addition of metabolites. Lactate and glycerophosphate had no such effect, nor was there any effect seen by the addition of glucose, glycerol or lecithin.

⁴ R. Mond, *Arch. ges. Physiol.*, 1927, 217, 618.

⁵ M. Koll-Schröder, *Arch. ges. Physiol.*, 1934, 234, 266.

⁶ L. V. Beck and R. Chambers, *J. cell. comp. Physiol.*, 1935, 6, 441.

The addition of methylene blue, however, which is known to enhance the otherwise low respiration of red cells considerably, suppresses the NaF effect, whereas the iodoacetate effect is only slightly affected. The same is true for the addition of NaCN. (It may be remembered, that NaCN is no antagonist of methylene blue, the methylene blue respiration is not affected by NaCN.)

It is not possible, so far, to make any suggestions as to a particular metabolite, whose presence or absence might be responsible for the effects described. The existence of a relation between maintenance of selective anion permeability and metabolism, however, seems to be established.

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THE PERMEATION OF HUMAN ERYTHROCYTES BY ANIONS AND CATIONS.

BY MONTAGUE MAIZELS.

Received 1st March, 1937.

The non-nucleated mammalian erythrocyte is of special interest to biologists because in spite of its simplicity it presents several problems relating to semipermeability. It is permeable to anions and not to cations. Yet it contains a high concentration of cation and must have been permeable to cation at some stage in its development. But even at this stage permeation must have been anomalous for while the sodium concentration of the plasma environment is 155 m.eq., compared with only 5 m.eq. of potassium, the potassium concentration of the human erythrocyte is 160 m.eq. while that of sodium is 15 m.eq. These are matters which are of importance because they are doubtless linked up with cell development, maturation, senescence and destruction.

It is generally held that red cells consist of a membrane composed of lipid and a protein isoelectric at p_H 5, which encloses a solution of hæmoglobin and salts. In considering problems of permeability, it must be remembered that cells in drawn blood, and especially in unphysiological solutions like saline, cannot be compared to cells in the circulating blood; some trauma must occur, and the time factor in experiments is important.

Although the effective cell membrane is of extreme thinness, perhaps unimolecular,¹ and probably not more than two or three molecules thick,² diffusion is not immediate. Even chloride equilibrium is a matter of minutes and in the case of slowly diffusing substances there is a measurable temperature coefficient. Thus, in the case of cells suspended in phosphate solution for five minutes the coefficients are as follows: 0-10°, 1.4; 10-20°, 1.6; 20-30°, 2.5; 30-40°, 1.3. The same coefficients hold for cold-blooded animals like the frog. For the inward diffusion of glucose from a 7 per cent. solution, the temperature coefficient is 1.3

¹ Fricke, *Physiol. Rev.*, 1925, 26, 682.

² Danielli, *J. Gen. Physiol.*, 1935, 19, 19.

between 10 and 20° and 2.2 between 20 and 30°, while for the outward diffusion of potassium into an external sugar solution the corresponding coefficients are 1.1 and 2.2. There are many such biological processes of an apparently physical nature where the magnitude of the temperature coefficient suggests a chemical basis. However, Danielli³ has shown theoretically that for thin films, as the power of a substance to penetrate decreases so the temperature coefficient increases and may reach a relatively high figure.

Water penetrates more rapidly than ions. This may be shown by suspending cells in alkaline hypotonic saline. There is first some swelling due to an inflow of water from the low external to the high internal osmotic pressure; this is quickly followed by cell shrinkage which results from the outflow of water consequent on loss of chloride accompanying the increase in cell p_H .

It cannot be shown that hydrogen ions diffuse faster than the fastest anion, since ions cannot diffuse alone, and while the rapid permeation of water may be due to H and OH diffusing faster than other ions, it may also be due to H₂O diffusing more rapidly in the undissociated state. Jacobs⁴ suggests that H⁺ like other cations penetrates erythrocytes with difficulty and produces evidence to show that cell equilibrium is reached through the adjustment of OH ions.

Permeation of Anions.

A simple method of comparing the permeation rates of anions⁵ consists in suspending a known volume of centrifuged erythrocytes in 100 volumes of a solution containing equivalent amounts of KCl and a second salt KA. After five minutes, the suspension is centrifuged and the Cl content of the cells estimated. The value of A is determined directly or indirectly. Under these conditions an inequality in the distribution of Cl and A may occur in one of two ways:

(1) A stable inequality may result, independent of p_H and due either to a difference in ionic activities within and without the cells or possibly to one of the anions forming a complex with the cell constituents. Thus in normal blood, if r_H is the ratio of the hydrogen ion concentrations in cell and plasma, r_{Cl} the chloride and r_{HCO_3} the bicarbonate ratios, then⁶ $r_H = 0.7$, $r_{Cl} = 0.62$, r_{HCO_3} . Similarly, when bromide is added to plasma, a relative excess is found within the cells,⁷ while erythrocytes in a solution containing equivalent amounts of KCl and KI have an iodide content which is 20 per cent. greater than the chloride.

(2) An unstable inequality may exist, maximal at the outset and decreasing later. This arises as follows: if A⁻ permeates more readily than B⁻, it will enter the cell more rapidly either by exchanging with a proportion of pre-existing chloride or in combination with H ions if the external solution has been rendered more acid. Once A⁻ has combined with cell base, it is only slowly displaced by B⁻, whose permeation is apparently depressed. Thus chloride and salicylate both penetrate with great rapidity from solutions of single salts, equilibrium being reached in less than five minutes. But if cells are suspended in an acid solution containing salicylate and chloride in the ratio of 1/7, the ratio within the cells after five minutes is not 1/7, but 1.5/1. Thereafter, cell Cl rises and salicylate falls until at one hour the ratio is 1/2.4—a value still much in excess of the external ratio.

³ Danielli and Davson, *J. Cell. and Comp. Physiol.*, 1935, **5**, 495.

⁴ Jacobs, *Biol. Bull.*, 1932, **62**, 63.

⁵ Maizels, *Biochem. J.*, 1934, **28**, 337.

⁶ Van Slyke, *et al.*, *J. Biol. Chem.*, 1925, **65**, 701.

⁷ Hastings and Van Dyke, *ibid.*, 1931, **92**, 13.

If, then, erythrocytes are suspended in a series of solutions: KCl, KA; KCl, KB; KCl, KC . . . the various ratios A/Cl, B/Cl . . . are related to the permeation rates of A, B. . . . But A and B cannot be compared directly with Cl, since the untreated erythrocyte itself has a natural content of Cl, and so the various ratios are weighted in favour of Cl. This effect is naturally less evident at low p_H , where the acid binding power of the cells is increased, and more anions actually permeate from the exterior. But although A may not be compared directly with Cl, the ratios A/Cl, B/Cl, and hence A, B . . . may be compared with one another. Even so, the method is only semi-quantitative, since the ratio not only depends on the relative permeation rates of Cl and A, but also on the power of one anion to displace another or be displaced by it, and it further depends on relative activity or complex formation.

Bearing these limitations in mind certain conclusions have been reached: the permeation of inorganic anions follows a lyotropic series; the ratios for I, CNS, NO₃, Cl, SO₄ and PO₄ at p_H 7.0 being 1.24, 1.09, 1.09, 1.0, 0.21 and 0.15. It is probable that activity is at least as important in determining these ratios as permeation rate. In the case of organic anions the findings agree best with Jacobs' ⁸ exposition of Overton's views, that those substances permeate best which are least polar. Hence permeation varies directly with solubility in non-polar solvents and length of the carbon chain and inversely with the number of polar groups and degree of dissociation. These factors are to some extent interrelated. The effect on permeability of the length of the carbon chain is evident in the first five members of the mono-carboxylic acid series, and is best seen at low p_H . Here the anion ratio, R , increases from 0.8 for formate (p_K 3.7) and 1.6 for acetate (p_K 4.73) to 2.0 for valerate (p_K 4.8). This is probably related to acetate and valerate being poorly dissociated at p_H 5.1, for at p_H 7.0 the value of R for all five acids is the same 0.75. Indeed, it is possible that these organic acids permeate chiefly in the undissociated state—as acetic acid rather than acetate; but for the sake of simplicity the ion designation is retained throughout. In the dicarboxylic acids, malonate and succinate have ratios of 0.8; azelate, 1.47. Oxalate is an unexplained exception to this rule having the highest ratio of any acid 6.32 at p_H 5.1.

The introduction of polar groups into an acid lowers its solubility in non-polar solvents, usually increases its dissociation, and delays permeation. Thus at p_H 7.0 the permeation rates of acetate, malonate, glycolate, lactate and tartrate are respectively 0.8, 0.35, 0.30, 0.30, 0.15. It is interesting to note that α -hydroxypropionate (p_K 3.85) is strongly dissociated and penetrates slowly while the β -acid (p_K 4.61) penetrates rapidly, the values for R being 0.69 and 1.16 at p_H 5.1. The same observations apply to the aromatic acids, even the complex naphthoate penetrating very rapidly. It may be remarked that *o*-hydroxybenzoate penetrates rapidly and phenylhydroxyacetate slowly; the p_K , ether-water partition and R of these substances at p_H 5.1 being respectively 3.0, 5.0 and 1.78, compared with 3.37, 1.33 and 0.75. Here permeation appears to be more closely related to solubility in non-polar solvents than to non-dissociation. Solubility rather than non-dissociation appears to be operative in the following series: iodoacetate (p_K 3.15, R at p_H 5.1, 1.56), thiolacetate (p_K 3.55, R , 1.92) and *o*-hydroxybenzoate (p_K 3.0, R , 1.92) on the one hand, compared with formate (p_K 3.7, R , 0.8), acetate (p_K 4.73, R , 1.6) and benzoate (p_K 4.2, R , 1.48) on the other.

While the less polar anions penetrate more rapidly at low p_H , doubtless because of their greater solubility in the lipoids of the cell, the same increased permeation rate is observed in the well-dissociated acids like sulphuric and the hydroxy-organic acids. It may possibly depend on a decrease of the negative charge on the cell at low p_H .

⁸ Jacobs, *General Cytology*, Section 3, Chicago, 1924.

The Permeation of Cations.

It is possible that in the circulating blood a gradual interchange of cation occurs between cell and plasma; and *in vitro*, if the conditions are sufficiently unphysiological. But human blood cells suspended in salt solutions appear to be relatively impermeable to cation. In KCl solutions containing 100 and 350 m.eq. per litre, the increase in cell K is 4 and 10 per cent. respectively, while in similar solutions of NaCl cell K decreases⁹ by 5 per cent. These changes are small and immediate; after the first minute or so, there is no further change in cell cation for periods up to four hours and in suspending solutions whose concentrations vary between 100 and 350 m.eq. It is suggested that these small changes are not due to cation penetrating the erythrocyte, but to an exchange of surface cation. In support of this view it may be recalled that the cell envelope consists of lipid and a protein, both of which are capable of binding base at p_H 7.0.

According to Mond¹⁰ cations permeate at p_H greater than 8.3. The present writer, using a solution containing 350 m.eq. KCl per litre, found that cell K was 111 m.eq. at p_H 8.3 and 115 m.eq. at p_H 8.7 compared with a natural original content of 101 m.eq. Such a solution is grossly hyper-tonic, and cell damage cannot be excluded. However, as cells have a natural K concentration of 160 m.eq., weaker KCl solutions cannot be used for demonstrating permeation. In the case of NaCl, cell K decreased by 4 per cent. at p_H 7.0, by 5 per cent. at p_H 8.7, and by 10 per cent. at p_H 9.5, so that increased permeation of cation is not evident in human cells at p_H less than 8.7. Davson and Danielli¹¹ criticise the technique of Mond's experiments. Mond suspended 1 volume of ox cells in 2.4 volumes of glucose solution made alkaline with NaOH and though the final p_H of such a system might be between p_H 8 and 9, the initial p_H is about 12.8, at which reaction cell damage is certain; and in fact Mond himself reports the occurrence of hæmolysis. The same criticism applies to the present writer's experiments—though with less force, since he suspended 1 volume of cells in 100 volumes of solution, so that the p_H gradient from the initial to the equilibrium point of the experiment was very much less and no hæmolysis was observed. However, it is possible that had buffered Ringer's solution been used, erythrocytes would have lost no more base at p_H 10 than at 7.0. Such, in fact, was the experience of Davson and Danielli¹¹ with rabbit cells suspended in buffered Ringer solution.

Human and rabbit red cells therefore appear to be practically impermeable to cation. Regarding other species: Kerr¹² found for dog, sheep, ox and man that cation penetrated cells suspended in salt solution, but that penetration was inhibited by the addition of serum. I have been unable to confirm the large changes observed by Kerr in human cells, while according to Davson¹³ serum does not inhibit permeation in the ox. It may be remarked that volume changes were not well controlled in Kerr's experiments. Using ox cells, Davson¹³ demonstrated a degree of cation permeation, but changes in cell cation were small when compared with the changes in composition of the suspending solution.

While human cells in electrolyte solution are almost impermeable to cation, in solutions of a non-electrolyte like glucose, a considerable loss of cell cation occurs, but this can be largely prevented by the addition of a small amount of electrolyte to the glucose. NaCl is as effective as KCl.

It might be thought that cation permeation is strong glucose solution depended on cell damage, and this is probable, since impermeability once lost in this way cannot be restored in salt solution. But glucose damage is not the only factor for the addition of only 11 m.eq. of NaCl or KCl greatly

⁹ Maizels, *Biochem. J.*, 1935, **29**, 1970.

¹⁰ Mond, *Pflüger's Arch.*, 1927, **217**, 618.

¹¹ Davson and Danielli, *Biochem. J.*, 1936, **30**, 316.

¹² Kerr, *J. Biol. Chem.*, 1929, **85**, 47.

¹³ Davson, *Biochem. J.*, 1934, **28**, 676.

delays cation loss, although the glucose content itself is unaltered. It seems probable that impermeability to cations depends in some way on the maintenance of a surface layer of ions and of some other constituent of the cell membrane, and that removal of the surface ions is accompanied by loss of this other constituent, since replacement of the cell in salt solution, though it may restore the surface ions, does not restore impermeability. The decrease in such a layer of surface ions accompanying a relatively large decrease in the concentration of ions in the suspending solution would be comparatively small, and since ions in the cell would be in equilibrium with the surface ions, cell cation also would decrease only slightly with decrease in the external ion concentration. In this way the figures in columns 2 and 3; 5 and 6 of Table I. might be explained.

TABLE I.—CELLS IN GLUCOSE SOLUTION WITH AND WITHOUT ADDED SALTS.
T = 30°. TIME = 60 MINS.

Extl. Glucose Per Cent.	Extl. K m.eq.	Cell K m.eq.	Extl. Glucose Per Cent.	Extl. Na m.eq.	Cell K m.eq.
0	175	111	0	175	100
6.1	22	99	6.1	22	92
6.5	11	87	6.5	11	84
6.8	5.5	71	6.8	5.5	68
7.0	0.75*	37	7.0	0.75*	37

(* K absent from original glucose but diffused out of cells.)

Discussion.

It is difficult to unite all these observations in one comprehensive theory. Mond's¹⁰ much quoted and attractive views must be rejected. He states that erythrocytes are only permeable to anion at p_H less than 8.3 and to cation at p_H greater. He postulates the presence of a cell globin isoelectric at about p_H 8. We have seen that under satisfactory experimental conditions cation permeation at p_H 8.7 and probably at p_H 10 is no greater than at p_H 8.3. Further anions do penetrate at high p_H ; for phosphate will diffuse inwards from a solution at p_H 10 and Cl will pass outwards, though the final anion content of the cell is decreased in accordance with the p_H requirements. Finally, there is no cell protein capable of acting in the way that Mond suggests.

According to Hober¹⁴ and others, the erythrocyte is negatively charged, and therefore cation and not anion should penetrate at p_H greater than 5. But the reverse is the case. It is therefore probable that neither adsorption nor penetration through a pore is the cause of cell semipermeability, but that the mechanism is one of passage through a lipid layer, where as Danielli and Davson¹¹ remark, the ϵ potential is the one of interest; "since in the case of the erythrocyte ϵ is probably always positive and not changed in sign by p_H changes, a reversal of ionic permeability with change of p_H is not to be expected." This mechanism agrees with the recorded observations on anion and cation permeation.

Serological agglutination of erythrocytes, however, shows that protein must be intimately associated with the true cell surface, though it is difficult to believe that it can play an important part in permeability.

¹⁴ Hober, *Pflüger's Arch.*, 1904, 101, 607; 102, 196.

For if distributed as a mosaic with lipid, it should permit the passage of cation, while if distributed over the lipid as a surface layer, it should impede the passage of lipid soluble compounds. It is, of course, possible that such a surface layer of proteins might be discontinuous, or that there are, in fact, two complete layers—a lipid and a protein, and that the combined permeability of these two favours the lipid soluble rather than the water soluble substances. In support of this, there are Mond's¹⁵ observations that the permeation of polar compounds, in contrast to that of the non-polar, decreases with increase in molecular size. The presence of such surface films would explain why permeation occurs more readily at low pH ; the lipid soluble acids penetrate because they are less dissociated and the dissociated anions like sulphate and tartrate because the protein film is less charged at low pH .

It is difficult to understand why the human erythrocyte developing in a medium containing so much sodium should yet maintain a very high potassium concentration. True permeation of the erythrocyte by cation cannot be demonstrated *in vitro* unless the cell is damaged by heat or by solutions that are grossly hypertonic, or acid or alkaline or electrolyte free. But if such damage is effected, even though it be so slight that less than 5 per cent. of the cells are hæmolyzed, then semipermeability is lost; phosphate penetrates as readily as chloride while cation permeation is free. If such damaged cells are exposed to a solution containing Na and K these enter in equivalent amounts; there is no elective permeation of K. It is possible that in the intact animal slow permeation of cation into the mature erythrocyte occurs, and that the spleen or some other organ reacts on the cell so as continually to reshuffle cation in favour of potassium. But it is more probable that the paradoxical distribution of potassium of cation has arisen during a stage in cell development. In this connection, the model of Osterhout and Kammerling¹⁶ is of interest. It consists in principle of a non-aqueous cresol guaiacol phase separating two aqueous phases. A containing LiOH and KOH and B containing water through which CO₂ bubbles. The latter determines a flow of base from A to B, while the greater solubility of K in guaiacol gradually leads to a relative excess of K and an absolute excess of base in B. The immature erythrocyte develops in the bone marrow. It is nucleated and its relatively high metabolic rate, together with specific physical or chemical attributes, may determine an inflow of K. Later in development, the nucleus is lost, CO₂ production becomes negligible, and the cell finally escapes from the bone marrow into the blood stream. This maturation process is in abeyance in the disease known as pernicious anæmia, but after the administration of liver extract it reappears. One may wonder if cell maturation under the influence of hæmato-poetic substances from the liver is in any way related to the impermeability of the erythrocyte to cation.

GENERAL DISCUSSION.*

Dr. J. F. Danielli (London) (communicated): Mr. Davson and I have made similar experiments to those of Dr. Wilbrandt, in which we estimated cations directly. We could find no trace of salt leakage due to any enzyme poison, including the ones used by Dr. Wilbrandt, with

¹⁵ Mond, *ibid.*, 1928, 220, 69.

¹⁶ Osterhout and Kammerling, *J. Gen. Physiol.*, 1935, 19, 167.

* On two preceding papers.

ox, rabbit, goose, or dogfish corpuscles. Nor was there any effect of methylene blue or pyocyanin. We have not worked with human cells, but we are none the less inclined to wonder whether Dr. Wilbrandt's indirect method has not misled him. Cannot the contraction which he observed be due to some cause other than salt leakage? For example, we have found that, in certain cases, centrifuging will cause a loss of up to 40 per cent. of the cell potassium!

Incidentally we have repeated Mond's work on the reversal of ionic permeability at p_H 8.3 on ox cells and dogfish cells, and cannot find any such reversal if proper conditions are used. (This is discussed by Dr. Maizels.)

Mr. O. Gatty (*Cambridge*) said: The effect of iodoacetate on frog skin potential is antagonised for a time both by lactate and by pyruvate. Preliminary observations indicate that it leads initially to an increase in electrical resistance and therefore to a decreased permeability to ions.

Professor Kurt H. Meyer (*Genthod Geneve*) said: The observation that "salicyl ions" in acid solution penetrate more rapidly into erythrocytes than chlorine ions, while in neutral solution the converse is true, may be explained by the fact that much undissociated salicylic acid will be present in acid solution, and this will be able to pass through the lipoids—which the ions cannot do.

Dr. T. Teorell (*Uppsala*) said: In connection with Dr. Maizels' interesting observations, that organic acids probably permeate the red cells in the undissociated state, I should like to quote some similar results which were obtained on living stomach mucosa. These results¹ showed that the weaker the acid the more rapidly did it diffuse out of the stomach content into the mucosa. In agreement with Dr. Maizels, one may suggest that solubility probably plays a certain rôle.²

Mr. O. Gatty (*Cambridge*) said: Dr. Maizels has asked about the action of oxalate. One possible reaction is, of course, precipitation of calcium and it would be interesting to compare results with those for citrate and tartrate which form complex ions with calcium. Oxalate and citrate are the only two anions so far discovered (tartrate not tried) which, when replacing chloride on the inside of frog skin set up between two solutions of Ringer at p_H 8, lead to negative potentials. The former ion is irreversible and the latter reversible in its effect; negative potentials are not observed with the calcium precipitants phosphate and fluoride. Thus the effect may not be due to mere removal of calcium. Citrate lowers the resistance on the inside of the skin but not when applied to the outside, and it could conceivably be obtained from all the substrates listed in a later paper as being capable of being oxidised to precursors of the potential. Thus citrate may be *the* respiratory precursor of potential. Citrate also has a marked action on nerve.

There is little doubt that frog skin is not abnormally permeable to potassium ions and that the latter cause an increased electrical conductance of the skin by a general increase in permeability rather than by their own abnormally high mobility. The evidence for this is written in Mr. Deans' introduction³ where it is suggested that potassium affects the permeability to anions to a greater extent than that to cations. In May, 1937, Mr. Dean obtained direct experimental evidence that anion mobilities and/or anionic adsorption are affected by potassium ion. These results come from observations of the "chloride-free effect"⁴ in potassium-rich Ringer. The results are markedly different from those in sodium

¹ See p. 920.

² However, the term solubility may rather be interpreted in the sense advanced by Schulman (p. 1141), *i.e.*, adsorption and "penetration" of surface films through a mechanism of ion-dipole or dipole-dipole associations. The former combination is of the order of ten times stronger than the latter. *Private suggestion by Dr. J. H. Schulman.*

³ See page 1053.

⁴ See page 1018.

Ringer, and it follows that potassium has profoundly altered the properties of the cell surfaces and their reactions to different anions.

Dr. W. Wilbrandt (*Bern*), in reply, said: As to Dr. Danielli's experiments, I wish to emphasise, that the assumption of salt leakage in my experiments has been checked by chemical analysis of potassium. The loss of potassium in the fluoride suspension was about ten times that of the control suspension. No centrifuging was involved in the procedure. Human cells seem to show the effect best. Of the cells mentioned by Dr. Danielli, I have used rabbit cells, which showed the same effect, but not so strongly as human cells. The reason for the discrepancy between Dr. Danielli's experiments and mine may be that he worked ⁵ at 25°, whereas my experiments were carried out at 37°.

Dr. M. Maizels (*London*), in reply, said: That as erythrocytes were calcium free, the rapid penetration of oxalate must be ascribed to other factors. Citrate and tartrate penetrated very slowly indeed.

⁵ *Personal communication.*

ELECTRIC IMPEDANCE OF MARINE EGG MEMBRANES.

By PROFESSOR K. S. COLE.

Received 1st March, 1937.

Soon after the announcement of Ohm's law in 1827, attempts were made to determine the direct current electrical resistance of biological materials. As methods became available, measurements were made with alternating current, first at low frequency and more recently at higher and higher frequencies. A similar development in the technique of interpretation of the data, led by Höber,¹ Philippson,² and Fricke,³ has evolved a fairly general picture of the electrical properties of living cell structures.

The cell membrane has a high resistance to direct current and low frequency alternating current, but the thickness and dielectric constant are such that it also acts as a condenser with a large capacity per unit area. From measurements at moderately high frequencies, where the current can flow through this membrane capacity, the cell interior is found to be a relatively homogeneous electrolytic conductor.

To put these interpretations on a quantitative basis, it is necessary to have an adequate analytical representation of the current flow around and through the cells. The theory of suspensions of spherical cells is rather simple and is directly applicable to marine eggs.

A convenient starting-point for the theory is the Maxwell equation ⁴ for the resistance of a uniform random suspension of homogeneous spheres in a uniform field,

$$\frac{1 - r_1/r}{2 + r_1/r} = \rho \frac{1 - r_1/r_2}{2 + r_1/r_2} \quad (1)$$

¹ Höber, R., *Arch. ges. Physiol.*, 1910, 133, 237; *ibid.*, 1912, 148, 189; *ibid.*, 1913, 150, 15.

² Philippson, M., *Bull. Acad. roy. Belgique, Cl. Sc.*, 1921, 7, 387.

³ Fricke, H., and Morse, S., *J. Gen. Physiol.*, 1925, 9, 137.

⁴ Maxwell, J. C., 1873, *Treatise on Electricity and Magnetism*, Clarendon Press, Oxford, Art. 314.

where r, r_1, r_2 are the specific resistances of the suspension, the suspending medium and the suspended spheres, respectively, and ρ is the volume concentration of the spheres. This equation is based on potential theory and has been developed also by Clausius, Mossotti, Lorenz, Lorentz, Rayleigh, and others. It has been extended to spheroidal particles,⁵ but has been shown to be not applicable in cases where permanent polarisations are found.⁶ At high volume concentrations the equation agrees with the data surprisingly well.

However, living cells may not in general be considered as homogeneous spheres and the equation can only be used in those cases where it is a reasonable approximation. If they are conducting spheres surrounded by a thin poorly conducting membrane, we find from the expression for the equivalent resistance, r_2' , of a two-phase sphere,⁷ $r_2' = r_2 + z_3/a$, where z_3 is the membrane impedance⁹ for a unit area of membrane and a is the radius. When r_3 and c_3 are the parallel resistance and capacity for a unit area of membrane, $1/z_3 = 1/r_3 + j\omega c_3$ where $j = \sqrt{-1}$ and $\omega = 2\pi$ times the frequency. Substituting the value for r_2' for r_2 in equation (1) and similarly replacing r by z , the impedance of the suspension,⁸

$$z = r_1 \frac{(1 - \rho)r_1 + (2 + \rho)(r_2 + z_3/a)}{(1 + 2\rho)r_1 + 2(1 - \rho)(r_2 + z_3/a)} \quad (2)$$

From r_0 , the specific resistance of the suspension at low frequency and r_1 , we may compute the volume concentration when we assume the membrane is non-conducting,

$$\rho_0 = 2(1 - r_1/r_0)/(2 + r_1/r_0).$$

But if the membrane is conducting at low frequency, $z_3 \doteq r_3$ and when $r_3 \gg r_1 a$ and $r_3 \gg r_2 a$ we have

$$(\rho - \rho_0)/\rho \doteq 3r_1 a/r_3 \quad (3)$$

To measure r_3 it is necessary to have an accurate independent measure of ρ . This is to be had by diluting the suspension with an iso-osmotic dextrose solution and making a conductance titration for the amount of suspending medium.¹⁰ In Fig. 1 are shown the results for a number of suspensions of unfertilised and fertilised *Hippoonö* eggs in sea-water.

The two volume concentrations agree to within the experimental error of about 1 per cent. and from equation (3) the membrane resistance must be greater than 25 ohms/cm.² If the resistance is as high as has been found¹¹ in plant cells, 10^4 to 2.5×10^5 ohms/cm.², the

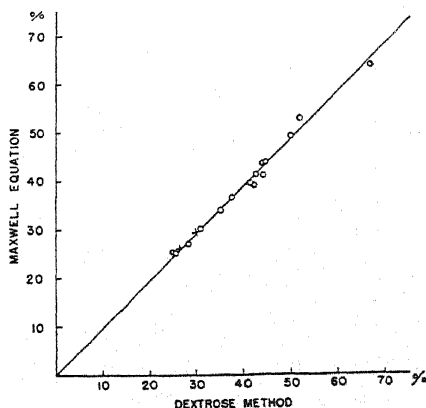


FIG. 1.—Volume concentrations of *Hippoonö* egg suspensions in sea-water.
o Unfertilised + Fertilised.

⁵ Fricke, H., *Physical Rev.*, 1924, 24, 575.

⁶ Onsager, L., *J. Amer. Chem. Soc.*, 1936, 58, 1486.

⁷ Maxwell, *loc. cit.*, Art. 313; Dänzer, H., *Ann. Physik*, 1934, 20 (5), 463.

⁸ Cole, K. S., *J. Gen. Physiol.*, 1928, 12, 29.

⁹ Wagner, K. W., *Ann. Physik*, 1913, 40, 833.

¹⁰ Cole, K. S., *J. Gen. Physiol.*, 1935, 18, 877.

¹¹ Blinks, L. R., *ibid.*, 1930, 13, 361; *ibid.*, 1930, 13, 495.

difference between the two volume concentrations would be about 0.002 per cent. ! Thus the membrane resistance of the cell is higher than it is possible to detect in these suspensions.

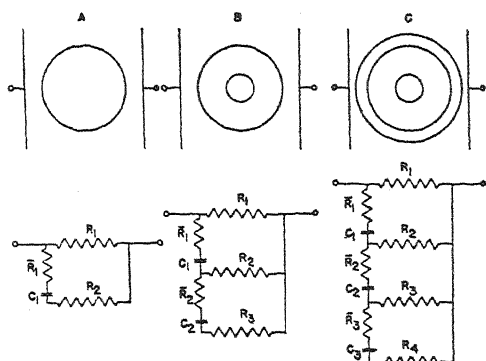


FIG. 2.—Postulated egg structures and their equivalent circuits. A has one alternate circuit,⁸ while B has 9 to 11 and C has 61 to 125.*

When the membrane may be considered as a non-conductor, $z_3 \doteq 1/j\omega c_3$, equation (2) is the expression for the impedance of the circuit of Fig. 2a. It is then found that the suspension or this network is equivalent at low frequencies to the parallel circuit of R_1 and C_1 , since \bar{R}_1 and R_2 may be neglected, and the membrane capacity is given⁸ by

$$c_3 = 2C_1 / (2 + r_1/r_0) \quad (1 - r_1/r_0)a.$$

This reduces at low volume concentrations to $c_3 = 2C_1/3(1 - r_1/r_0)a$, the expression obtained from the theory of suspensions of spheroids.¹²

For suspensions of *Hipponoë*, *Asterias*, and *Arbacia* eggs it was found that the parallel capacity was nearly constant at the lower frequencies, and the mean values of the membrane capacities calculated are as shown in the table.

	Unfertilised, $\mu f/cm.^2$.	Fertilised, $\mu f/cm.^2$.
<i>Hipponoë</i> ¹⁰	0.87	2.0
<i>Asterias</i> ¹³	1.1	—
<i>Arbacia</i> ¹⁴	0.73	3.1

To be certain that our picture is adequate and that the assumption of a single membrane is justified, it is necessary to take data at higher frequencies. From equation (2) we find

$$Z = R + jX = R_\infty + (R_0 - R_\infty)/(1 + j\omega\tau)$$

where R and X are the series resistance and reactance of a suspension, R_0 and R_∞ are the extrapolated series resistances at low and high frequencies, and the time constant of the suspension,

$$\tau = \left[\frac{1 + 2\rho}{2(1 - \rho)} r_1 + r_2 \right] c_3 a.$$

This equation may be represented in three dimensional space by curve I. of Fig. 3 where R , X , and $\log \omega\tau$ are the three co-ordinates. The projection of this curve on the R , $\log \omega\tau$ plane is

$$R = R_\infty + (R_0 - R_\infty)/(1 + \omega^2\tau^2)$$

given by curve II., and on the X , $\log \omega\tau$ plane,

$$X = -(R_0 - R_\infty)\omega\tau/(1 + \omega^2\tau^2),$$

* I am indebted to Mr. R. M. Foster of the Bell Telephone Laboratories for this enumeration.

¹² Fricke, H., *Physical Rev.*, 1925, 26, 678.

¹³ Cole, K. S., and Cole, R. H., *J. Gen. Physiol.*, 1936, 19, 609.

¹⁴ *Ibid.*, 625.

curve III. If, however, $\omega\tau$ is eliminated, the projection on the R, X plane is given by $(R - R_\infty)^2 + X^2 = (R - R_\infty)(R_0 - R_\infty)$ and curve IV. This is the well-known circle diagram or impedance locus¹⁵ which is widely used in power and communication engineering but is also a convenient representation of biological data.¹⁶

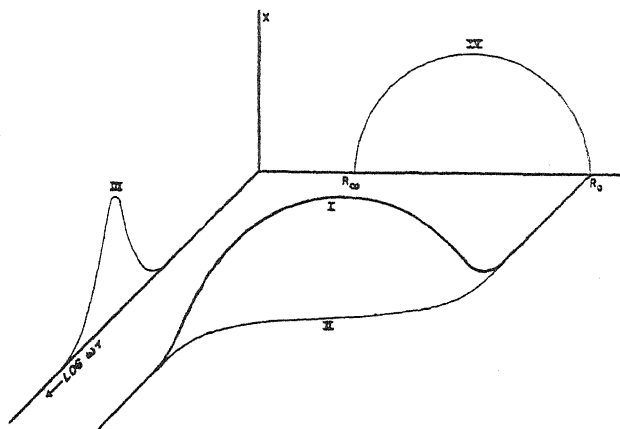


FIG. 3.—I. Complex impedance, Z , II. series resistance, R , and III. series reactance, X , vs. $\log \omega\tau$; IV. impedance locus, R vs. X .

For technical reasons it is usually convenient to balance the suspensions in a Wheatstone bridge against a parallel resistance and capacity and calculate the series resistance and reactance.

The impedance locus for a suspension of unfertilised *Asterias* eggs is shown in Fig. 4 for data from 1 kc. (kilocycle per second) to 16,000 kc. The circle represents the data fairly well at the low frequencies but shows a divergence at the high frequencies. It may be concluded that over the major portion of the frequency range the unfertilised eggs of *Hippoonö*, *Asterias*, and *Arbacia* behave like poorly conducting membranes of about one microfarad per square centimeter enclosing the cytoplasm having a specific resistance several times that of sea-water. Until the source of the high-frequency effect is located it is not possible to determine the internal resistance accurately, but for these three forms it is in the neighbourhood of 150 ohm cm.¹⁷

The question now arises as to whether or not the high-frequency effect may be due to the nuclear membrane. It is relatively easy to put a nucleus inside the egg, as shown in Fig. 2*b*, but the analysis of the data

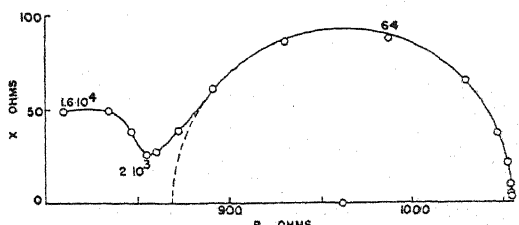


FIG. 4.—Impedance locus for 47.1 per cent. suspension of unfertilised *Asterias* eggs in sea-water. Frequencies in kc.

¹⁵ Campbell, G. A., *Tr. Am. Inst. Elect. Eng.*, 1911, 30, 873.

¹⁶ Cole, K. S., *J. Gen. Physiol.*, 1932, 15, 641.

¹⁷ Cf. Gelfan, S., *Protoplasma*, 1928, 4, 192.

is rather involved.¹⁸ We find that the new capacity element corresponding to the nuclear membrane is given by $C_2 = \frac{9\rho}{(2+\rho)^2} \cdot \frac{9\rho'}{(2+\rho')^2} c_4 a_4$, where c_4 is its capacity per unit area, a_4 the nuclear radius, and ρ' is the nucleus to egg volume ratio.

Extrapolating the data for the *Asterias* and *Arbacia* eggs to infinite frequency in a quite unjustifiable manner, it is found that if the high-frequency effect is due to membrane covered material, it would probably occupy about 5 per cent. of the egg volume. This is far too large for the nucleus and the effect may be due either to granules or some other microscopically recognisable component, or to protein or other large molecules in the cytoplasm or plasma membrane which have relaxation times of about 10^{-8} seconds.

Turning now to the fertilised eggs, we find that the low frequency data have given membrane capacities of 2 and $3\mu\text{f}/\text{cm}^2$ for the *Hipponoë* and *Arbacia* respectively. From these data alone it is not possible to say whether these are the capacities of the plasma membranes after

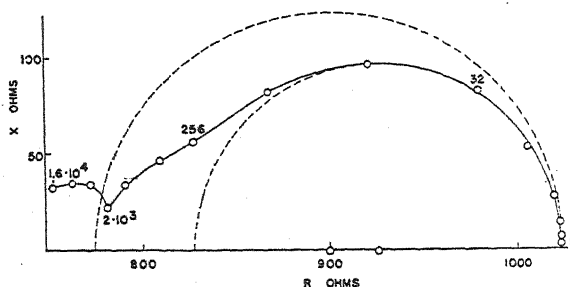


FIG. 5.—Impedance locus for 42.8 per cent. suspension of fertilised *Arbacia* eggs in sea-water. Frequencies in kc.

fertilisation, or the fertilisation membranes, or the resultants of both. Turning to the high-frequency data in Fig. 5 on fertilised *Arbacia* eggs, it is immediately seen that there is a considerable change in the impedance locus which suggests the entrance of yet another capacity element. Guided by the known microscopic structure, we may set up the picture shown in Fig. 2c to take account of the fertilisation membrane and the perivitelline space, and we obtain the equivalent circuit shown. From this assumption, the low-frequency capacities given are actually those of the fertilisation membranes. Assuming perivitelline spaces of 1μ and 1.5μ respectively for the *Hipponoë* and *Arbacia*, the specific resistance of this space in both cases is that of sea-water. It is difficult to obtain values for the plasma membrane capacities but after rather tedious reductions they are found to be unchanged within the rather wide limits of experimental error.

These interpretations have been represented diagrammatically in terms of current flow in Fig. 6. At frequencies below 1 kc., the current flows entirely around the unfertilised and fertilised eggs. In the neighbourhood of 50 kc. there is still very little current flow through the plasma membrane of either the unfertilised or the fertilised egg, but there is considerable current passing through the fertilisation membrane

¹⁸ Carter, C. W., Jr., *Bell. Sys. Tech. J.*, 1925, 4, 1.

and perivitelline space. As the frequency is raised to about 1000 kc., the current density in the plasma membrane and cytoplasm increases without involving the unknown structure. The effect of this structure reaches its maximum at about 16,000 kc.

It should be noted that all eggs in the suspension have been assumed to have identical properties. It is found¹⁹ that if there is any variation of the product c_3a in the suspended eggs, the impedance locus will be less than a semi-circle and its centre will be below the resistance axis.¹⁶ The loci shown have their centres on the resistance axis and we may conclude that there is no variation of c_3a . The standard deviation of the radii of eggs from a single female may be as low as 1 per cent. of the mean and the deviation of the membrane capacities must then be of the same order of magnitude.

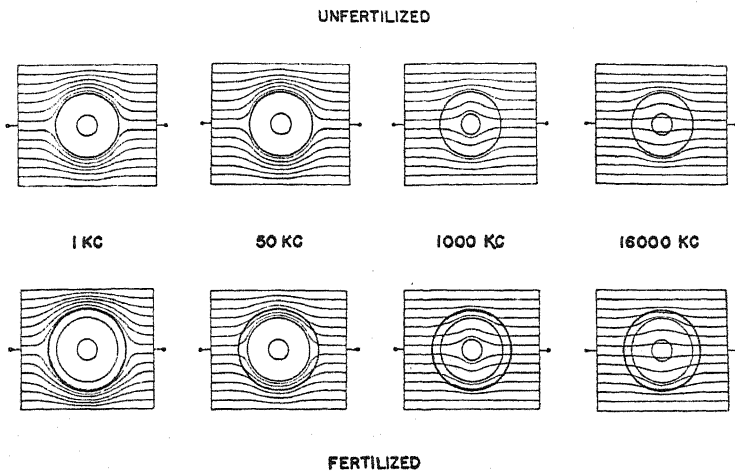


FIG. 6.—Schematic lines of current flow through suspensions of unfertilised and fertilised eggs in sea-water at frequencies indicated.

A few experiments on the capacity of *Hippoonœ* eggs swollen in dilute sea-water have shown that the membrane capacity per unit area decreases as the total surface area increases. Until more is known about the structure and behaviour of cell membranes, it is difficult to interpret this fact.

In an earlier paper²⁰ on *Arbacia* eggs, it was concluded that the membrane must be represented by a polarisation impedance and that that were no changes on fertilisation. It has not been possible¹⁴ to completely explain these results which certainly misled me and perhaps others.

Experiments on centrifuged masses of eggs at low frequency have shown the parallel resistance to be considerably lowered after fertilisation.^{21, 22} This has been interpreted as the result of a decrease in membrane resistance and has been taken as evidence of an increase in ionic permeability on fertilisation. The results on suspensions show that the

¹⁹ Cole, K. S., and Curtis, H. J., *Cold Spring Harbor Symposium*, 1936, 4, 73.

²⁰ Cole, K. S., *J. Gen. Physiol.*, 1928, 12, 37.

²¹ McClendon, J. F., *Am. J. Physiol.*, 1910, 27, 240.

²² Gray, J., *Phil. Trans. Roy. Soc., B*, 1916, 207, 481.

resistance of such a system depends upon several factors, and I do not feel competent to choose the most important one.

Summary.

The analysis of alternating current impedance data over a wide frequency range gives the electrical characteristics of several components in the eggs of marine forms. It is found that the membrane resistances of unfertilised and fertilised *Hipponoë* eggs are greater than 25 ohms/cm.² The unfertilised egg plasma membrane capacities in $\mu\text{f/cm.}^2$ are: *Hipponoë*, 0.87; *Asterias*, 1.1; *Arbacia*, 0.73. The *Hipponoë* membrane capacity decreases when the egg is swollen in dilute sea-water. In fertilised eggs, the fertilisation membrane capacities are: *Hipponoë*, 2.0; *Arbacia*, 3.1; while the plasma membrane capacities are apparently unchanged. At frequencies above 1000 kc. an unidentified structure becomes important in both the unfertilised and fertilised eggs.

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THE PROPERTIES OF THE GILL MEMBRANES OF FISHES.

BY ANCEL KEYS.

Received 2nd March, 1937.

In the gills of fishes there is a large surface of delicate membrane, from one to at most a few cells in thickness, separating the blood from the external environment. Knowledge as to the properties of this membrane proceeds from: (1) Physiological deductions, (2) morphological studies, (3) direct experimental observations.

In all the fresh water fishes and in the marine teleosts these two liquids—blood and external medium—are greatly different in osmotic pressure. In the marine elasmobranchs (sharks and rays), though the total osmotic pressure of the blood is closely similar to that of the sea water, about a third of the blood osmotic pressure is contributed by urea, a substance which usually penetrates biological membranes with great ease. These osmotic relations are summarised in Table I.

Physiological Deductions.

A large and constant difference in osmotic pressure between the blood and the external medium implies a mechanism for creating and maintaining this difference. The fresh-water fishes must perform osmotic work to conserve salt and exclude excess water, whereas osmotic work to conserve water and exclude excess salt must be done by the marine fish. Euryhaline fishes like the eel, salmon, and stickleback, are able to carry out both types of osmotic regulation, depending on whether they are living in fresh or salt water.

In the marine fishes it is conceivable that the low salt concentration of the blood relative to sea water might be maintained, in spite of gill membranes relatively permeable to salts and water, by the performance of an heroic amount of osmotic work elsewhere in the body—there is an abundance of salt and water at hand from which a blood of proper salt concentration could be elaborated. Impermeability to sugar and amino acids, however, is a metabolic necessity and, in the elasmobranchs, the

TABLE I.—OSMOTIC PRESSURES OF BLOOD AND EXTERNAL ENVIRONMENTS IN FISHES, TOGETHER WITH APPROXIMATE INDICATIONS AS TO THE PROPORTION OF THE TOTAL OSMOTIC PRESSURE CONTRIBUTED BY UREA. OSMOTIC PRESSURES IN TERMS OF FREEZING-POINT DEPRESSIONS (Δf) IN ° C.*

Form.	Δf of Environment.	Δf of Blood.	Δf Due to Urea as Per Cent. of Total Δf of Blood.
Cyclostomes			
Hag fish (<i>Polistotrema</i>) . . .	1.8 to 2.4°	1.8 to 2.4°	< 1
Lamprey (<i>Petromyzon fluviatilis</i>) . . .	0.01 to 0.1°	0.52 to 0.56°	< 1
Lamprey (<i>P. marinus</i>) . . .	1.8 to 2.4°	circa 1.0°	< 1
Elasmobranchs			
Marine sharks and rays . . .	1.8 to 2.4°	1.9 to 2.5°	circa 35
Estuarine forms . . .	1.0 to 1.5°	1.2 to 2.0°	37 to 45
Fresh water forms . . .	0.02 to ?	0.90 to 1.02°	19 to 23
Dipnoans			
Lung fish (<i>Protopterus</i>) . . .	0.03°	0.48°	< 0.05
Teleosts			
Fresh water fishes . . .	0.02 to 0.1°	0.50 to 0.57°	0.05 to 0.5
Marine fishes . . .	1.8 to 2.4°	0.65 to 0.85°	0.3 to 0.8
Euryhaline fishes (eel) . . .	0.02 to 0.1°	0.56 to 0.64°	< 1
" " (") . . .	1.8 to 2.4°	0.65 to 0.74°	< 1
" " (salmon) . . .	0.02	0.63°	< 1
" " (") . . .	2.0°	0.76°	< 1

* Compiled from data given by Bottazzi (1897, 1908); Rodier, E., *Trav. lab. stat. zool. Arcachon*, 1899, 103; Dekhuijzen (1904); Denis, W., *J. Biol. Chem.*, 1913, 16, 389, 1922, 54, 693; Greene, C. W., *Bull. U.S. Bur. Fish.*, 1904, 24, 429; Quinton, R., *C.R. Acad. Sci., Paris*, 1904, 131, 905, 952; Fredericq, L., *Arch. Biol.*, 1905, 20, 709; Dakin, W. J., (a) *Biochem. J.*, 1908, 3, 258, (b) 1908, 3, 473; Garrey, W. C., *Biol. Bull.*, 1905, 8, 257, 1915, 28, 977; Wilson, D. W. and Adolph, E. F., *J. Biol. Chem.*, 1917, 29, 405; Portier and Duval (1922); Schmidt-Nielsen (1923); Duval^{2a}; Smith, H. W.^{3a, 3b, 7} 1935, *Biol. Rev. Camb. Philos. Soc.*, 1936, 11, 49; Fontaine, M., *C.R. Acad. Sci.*, 1930, 191, 796; Keys,⁵; Boucher-Firly, S., *Bull. Inst. Oceanog. (Monaco)*, 1934, 651, 7; Grafflin.^{4a}

great concentration of urea in the blood demands the conclusion that this compound, ordinarily so highly diffusible, is likewise very largely restrained. In the fresh water fishes the paucity of salts available to the fish necessitates the conclusion that the salts also are restrained from diffusion from the gills.

Unless the skin is injured it is a matter of indifference to the fish what is the osmotic pressure of the medium which bathes its external surface: the determining factor is the fluid which enters the mouth and bathes

the gills.¹ If the gills of a fresh water fish are bathed in sea water, while the rest of the body is bathed in fresh water, the fish becomes dehydrated and dies. Similarly in the sea water fish in sea water but with its gills bathed by fresh water; it swells, becomes water-logged and dies. The reversed condition—the proper medium on the gills and the unfamiliar medium on the body—produces no untoward effect.² It is clear that when the fish is in its normal osmotic environment the gill membrane is relatively resistant to passive exchanges of salt and water; when the normal osmotic gradient across the membrane is reversed this impermeability is destroyed except in the euryhaline fishes. The general body surface is important only as an armour impermeable to all exchanges.

The activity of the kidney must be studied in order to make deductions concerning the branchial exchanges. The urine of the fresh water fish is relatively copious, very dilute (Δf generally less than 0.1°C.) and contains remarkably little urea, chloride, sodium and potassium.³ Qualitatively, and probably quantitatively, the kidney of the fresh water fish can account for all the needed osmotic work. The relative lack of urea in the urine suggests that it may be eliminated in part by passive diffusion from some extra-renal source such as the gills. The same may also be true of chloride, sodium, and potassium.

In the marine teleosts the situation is very different. The urine is scanty in volume, isotonic or hypotonic to the blood (never hypertonic), and it contains relatively little urea. Chloride, sodium and potassium are present in surprisingly small concentration, but the output of calcium magnesium and sulphate in the urine is relatively large.^{3, 4} To explain these findings we must conclude that *extra-renal* osmotic work is done by the marine teleost; the gills may be the site of this activity.^{4a}

The rôle of the gastro-intestinal tract must likewise be evaluated. In the fresh water fish this question is quickly eliminated. The fresh water fish never "drinks" and the external medium enters the gastro-intestinal tract only in small amounts incidental to the swallowing of food.^{3b, 5} The sea water fish, however, continually "drinks" sea water.^{3a, 4e, 6} By analysis of the fluid in various parts of the gastro-intestinal tract, Smith^{3a} showed that only passive absorption takes place; in the lower parts of the tract the gut contents approach isotonicity with the blood. However, in this passive osmotic exchange the smaller molecules—Cl, Na, K—are absorbed much more readily than Ca, Mg and SO_4 . It is apparent that the major osmotic work in the marine fish must involve extra-renal and extra-gastro-intestinal secretion. Smith's calculations show that the chlorides of sodium and potassium are the substances to be accounted for in this way; Ca, Mg, SO_4 and probably PO_4 are taken care of by the kidney.

¹ (a) Bert, P., *C.R. Acad. Sci. (Paris)*, 1883, 97, 133. (b) Regnard, P., *La vie dans les eaux*, Paris, 1891.

² (a) Duval, M., *Ann. Inst. Oceanog. (Monaco)*, 1925, 2, 233. (b) Sumner, F. B. *Bull. U.S. Bur. Fish.*, 1906, 25, 53.

³ (a) Smith, H. W., *Am. J. Physiol.*, 1930, 93, 480. (b) Smith, H. W., *Quart. Rev. Biol.*, 1932, 7, 1.

⁴ (a) Bottazzi, F., *Arch. Fisiol.*, 1906, 3, 547. (b) Burian, R., *Pflüger's Arch.*, 1910, 135, 741. (c) Dekhuyzen, M. C., *Arch. neerland Sci.*, 1905, 10, 121. (d) Grafflin, A. L., *Biol. Bull.*, 1935, 69, 245. (e) Grafflin, A. L. and Ennis, D., *J. Cellular Comp. Physiol.*, 1934, 4, 283. (f) Marshall, E. K., Jr., and Grafflin, A. L., *Amer. J. Physiol.*, 1928, 85, 391. (g) Pitts, R. F., *J. Cellular Comp. Physiol.*, 1934, 4, 389.

⁵ Keys, A., *Proc. Roy. Soc. B*, 1933, 112, 184.

⁶ Keys, A., and Willmer, E. N., *J. Physiol.*, 1932, 76, 368.

We are left, then, with the branchial cavity in which to find: (1) passive diffusion of urea from the blood of both marine and fresh water fishes, (2) passive diffusion of small amounts of Na, K, and Cl from the blood of fresh water fishes, (3) active secretion of Na, K, and Cl from the blood of marine fishes. The latter process requires the performance of a large amount of thermodynamic work and is of vital importance in the preservation of the homeostasis of the organism. As Smith^{3b} suggests, we should expect this process to be associated with an abundant blood supply such as the gills receive. Other structures in the oral cavity do not bring the blood into close contact with the external environment nor are they prominently placed in the circulatory system.

The weight of inference is in favour of the gills as the responsible agents for the osmotic work. The argument for the localisation of the passive diffusion of urea in all teleosts, and of water,* Na, K, and Cl in fresh water forms, in the gills, is stronger. The gill membrane is exceedingly thin, delicate, and filled with rapidly circulating blood; the oral mucous membranes are very thick, dense, coated with mucous, and poorly supplied with blood. Finally, the extent of surface for exchange afforded by the gills is many times as large as that of all the rest of the branchial cavity.

A differentiation of exchanges in different parts of the body of the fresh water fish may be made by placing the fish in a divided box so that the anterior (including the branchial cavity) and posterior part of the body are effectually separated with regard to the external medium. A separation of skin and renal exchanges in the posterior part of the body may be made by placing a retention catheter in the ureter. Such experiments have been made by Smith⁷ who reported that in the fresh water fish a small loss of Na, K, and Cl takes place from the anterior end of the animal when the concentration of these salts in the body is raised artificially, but that the general body surface is impermeable. Extra-renal excretion of nitrogen from the anterior part of the body can also be demonstrated in this way. I have confirmed these general findings by similar experiments. These passive exchanges must not be confused with the secretory processes, requiring thermodynamic work, involved in the water economy of the marine teleosts.

Direct Observations.

The properties of the gills may be more directly studied in the heart-gill or pump-gill preparation of the fish.⁸ In these preparations the gills are perfused, either from the beating heart or from the ventral aorta (using a perfusion pump).⁹ The outflow is collected from the dorsal aorta cannulated close to the efferent vessels. In the eel it is possible also to arrange a non-leaking perfusion of the branchial chamber. With this arrangement an isolated system is set up in which, with appropriate chemical methods, the fluids entering and leaving the branchial chamber and the fluids entering and leaving the gills can be compared. It should be noted that, though

⁷ Smith, H. W., *J. Biol. Chem.*, 1929, 81, 727-742.

⁸ Keys, A., *Z. vergl. Physiol.*, A, 1931, 15, 352.

⁹ See Bateman, J. B., and Keys, A., *J. Physiol.*, 1932, 75, 226.

* The fasting fish in fresh water continues to secrete urine even though no water is swallowed and the body weight is practically constant. As the skin is normally impermeable we must admit that water diffuses into the body in the oral cavity.

the gills are not removed from the body, they are isolated from the rest of the head.*

When such a preparation is made with the surviving eel head (*Anguilla vulgaris* from fresh water) perfused with Ringer's solution isotonic with the blood ($\Delta f = 0.58^\circ \text{C.}$) and with fresh water in the branchial chamber, the perfusate collected from the dorsal aorta will be found to be slightly diluted, while there is a corresponding increase in concentration of the outer medium.¹² A tendency towards passive equilibration is observable and careful analytical technique, with measurement of inflowing and outflowing volumes in the two perfusion systems, permits quantitative estimation of the permeability of the membrane to various substances.

The results of these experiments¹³ are clear-cut. The gill membrane is passively permeable, in decreasing degree, to ammonia, urea, water and to chloride; it is impermeable to sulphate, iodide, ferrocyanide, thiocyanate, iodate and probably to sugars (glucose and sucrose).

It should be noted that these conclusions only refer to the changes that can be detected with the best analytical methods as yet available. With care we can estimate a change in fluid volume (inside or outside) as little as 0.1 per cent.; the limit of analytical accuracy in the chloride method is about 0.01 per cent. Iodide, iodate, thiocyanate, and ferrocyanide can be detected in extreme dilution; used in this way a diffusion of perhaps as little as 0.01 per cent. of the amount experimentally introduced could have been detected. With the sugars, not only are the analytical methods less sensitive, but possibilities of local carbohydrate metabolism render the results rather uncertain.

It might be suggested that the gill membranes are abnormal and therefore unusually permeable in these preparations. This possibility cannot be entirely ruled out, though the gills themselves are certainly never injured mechanically nor can anoxaemia¹⁴ be a factor, even in Schlieper's experiments with a slow rate of external flow. Perhaps the best proof of the "vitality" of the gills under these conditions is to be found in the results where relatively high concentrations of internal perfusion medium are used.

In this case we imitate the condition of the eel in sea water— Δf of

¹⁰ Cf. Bevelander, G., *J. Morph.*, 1935, **57**, 335.

¹¹ Grant, R. T., and Regnier, M., *Heart*, 1926, **13**, 285.

¹² Keys, A., *Z. vergl. Physiol.*, **B**, 1931, **15**, 364.

¹³ (a) Keys, A., *Bull. Scripps Inst. Oceanog., Tech. Ser.*, 1931, **2**, 417, and unpublished studies. (b) Bateman, J. B., and Keys, A., *J. Physiol.*, 1933, **77**, 271. (c) Schlieper, C., *Z. vergl. Physiol.*, 1933, **18**, 682. (d) Schlieper, C., *Z. vergl. Physiol.*, 1933, **19**, 68.

¹⁴ See Landis, E. M., *Amer. J. Physiol.*, 1928, **83**, 528. Marshall, E. K., Jr., and Smith, H. W., *Biol. Bull.*, 1930, **59**, 135.

* The anatomical details are given by Keys and Willmer,⁶ but some notes here may not be amiss in view of some apparent misconceptions.¹⁰ Between the ventral aorta and the place of cannulation of the dorsal aorta there are the following points of egress from the branchial vessels: (1) the coronary artery, which arises from the 4th (sometimes also the 3rd) efferent vessel, (2) small antero-ventral prolongations of the anterior efferent vessels which supply the floor of the mouth, the lower jaw and the thyroid, (3) anterior prolongations of the dorsal aorta supplying the brain and upper part of the head. Ingress can only be gained by back flow or diffusion from these vessels. In the perfused preparation the coronary is completely blocked in the pump-gill preparation but no difference is seen when it is not specially tied off. The venous drainage from the head takes place into the sinus venosus, mostly by way of the anterior cardinal sinus; in all the perfused preparations the anterior and the posterior cardinal sinuses are tied off with the sinus venosus. It should be noted that the coronary veins drain into the sinus venosus.¹¹ As a final precaution the entire tissue surface where the head is severed from the body (at a level immediately posterior to the heart), as well as the ventral derivatives of the efferent vessels, may be coagulated with the actual or the electric cautery—with no influence on the experimental results.

internal medium = 0.65 to 0.75°C ., Δf of external medium 1.8 to 2.0°C . Here it is found that an exchange of chloride takes place in opposition to the concentration gradient. This is not in any way the result of a Gibbs-Donnan equilibrium; thermodynamic work of considerable intensity and amount is done.^{13a} The summarised data of a typical experiment are given in Table II.

TABLE II.—EXPERIMENT WITH DOUBLE PERFUSION PREPARATION OF EEL GILL. EEL FROM SEA WATER. TOTAL TIME OF PERFUSION 2 HOURS AND 21 MINUTES. TEMP. 13.5°C .

	Internal System.		External System.	
	<i>Inflow</i>	<i>Outflow</i>	<i>Initial</i>	<i>Final</i>
Vol. (c.c.) . . .	291.79	291.52	130.52	130.85
[Cl](m.Eq./L.) . . .	196.18	194.81	532.91	535.00
	<i>Loss</i>		<i>Gain</i>	
Vol. (c.c.) . . .	0.29		0.33	
Cl(m.Eq.) . . .	0.456		0.449	
	<i>Calculated Secretion</i>		<i>Calculated Secretion</i>	
	(Internal System Data)		(External System Data)	
	1570		1360	
[Cl](m.Eq./L.) . . .				
Thermodynamic Work, in Calories :				
Transport of XCl . . .	0.368		0.362	
" " H ₂ O . . .	- 0.119		- 0.135	
Net Cost . . .	0.249		0.227	

Mean minimum thermodynamic work:

= 0.151 calories per hour per gm. of gill tissue.

This result, confirmed by Bateman and Keys⁹ and by Schlieper¹³ invests the gills with a special interest. The only tissue in the vertebrates¹⁴ heretofore known to be able to form a hypertonic (in osmotic terms) secretion is the mammalian kidney.* The result is the more surprising in that the gills are relatively simple in structure. However, the agreement between the direct observation and the physiological necessity for this osmotic work leaves no doubt that this activity plays a vital and a continuous rôle in the marine teleosts.

The details of this secretory activity are only partly known. Simultaneous chloride and vapour pressure measurements show that chloride is secreted in company with a monovalent kation of approximately the same activity as sodium, from which it is inferred that only chloride, sodium and perhaps a little potassium are secreted.^{13b} There is always a movement of an appreciable amount of water so that the net result is the appearance of secretion of a very concentrated solution (up to $2N$ in Cl).

Schlieper^{13a} has suggested that the water movement may simply be a result of osmosis and that only pure NaCl is secreted. Schlieper cites the fact that when both internal and external concentrations are about 0.7°C . in Δf , the secretion of Cl is marked but there is no, or only very small, volume change in the two perfusates. This point must be left unsettled for several reasons: (1) the final accuracy of Schlieper's few observations is dubious in view of the great technical difficulties, (2) when internal and external fluids are isotonic the osmotic work diminishes almost to zero,

* This does not mean that other tissues are unable to do osmotic work as stated by Bevelander.¹⁰

so the physiological activity may not be comparable with the more normal condition. In any case, whether the water is actually secreted or merely diffuses out, the thermodynamic result is the same and the change in free energy must be calculated as done by Bateman and Keys.⁹

The osmo-regulatory power of the gill is most clearly shown when, with sea water ($\Delta f = 1.8$ to 2.4°C.) outside, the gills are perfused with varying concentrations of NaCl in the internal medium. At $[\text{NaCl}]$ about 0.14 N (Δf of the medium about 0.50°C.) there is little or no secretion, but as $[\text{NaCl}]$ is increased, the secretory activity begins at about 0.15 N and shows a response like the mammalian kidney to change in chloride concentration in the plasma. A rise of chloride concentration in the gills of the eel from 0.16 to 0.17 N may, for example, increase the chloride secretion to $10 \text{ mg. per hour per kilogramme}$ from an original level of 3 mg. , and at 0.20 N Cl the secretion will be between 20 and $30 \text{ mg. Cl per hour per kg. of fish.}$

The Mechanism of Secretion by the Gill.

It is certain that the secretory activity is little, if at all, affected by the concentration of the external medium, but is under sensitive control by the concentration of the internal medium. So far there would be four possibilities as to what might be the stimulating agent in the internal medium: (1) the total osmotic pressure, (2) the total ionic concentration (" μ ," the ionic strength), (3) the sodium concentration, (4) the chloride concentration.

Differentiation between these possibilities has been made by Schlieper^{13c} and by myself (unpublished results). When the gills are being perfused with a relatively dilute Ringer's solution, $\Delta f = 0.5$ to 0.6°C. , a change to Ringer's solution more concentrated in NaCl produces a marked rise in the chloride secretion. When this same experiment is made with a second Ringer's solution, which has been increased in osmotic pressure by the addition of glucose, sucrose, or urea, there is no change in chloride secretion. Similarly, when osmotic pressure, ionic strength, and Na concentration are elevated by the addition of NaNO_3 or Na_2SO_4 , there is little change in chloride secretion. It is clear that chloride, alone or in the company of sodium, is the specific stimulating agent and that we have to do primarily with chloride and not osmotic regulation.

The ultimate source of the energy required to affect the secretion is a matter of some importance. The oxidative metabolism of the intact perfusion preparation could, conceivably, be measured at various rates of secretory activity but the technical difficulties are formidable. A less direct approach is readily made by the study of the metabolism of the excised gills in Barcroft respirometers.⁹

The conditions of internal concentration which maintain the gills active or passive as regards secretion can be brought about readily with the extirpated gills. With the perfusion technique the gills may be filled *in situ* with fluid of any desired concentration. When these gills are extirpated and suspended in an appropriate solution, diffusion and osmotic interchange through the open (cut) ends of the gill bar and those membrane surfaces which are slightly injured by handling will tend to keep the concentration high or low, depending on the concentration of the external solution. Such experiments may be made with the gills on one side of the eel filled with Ringer's solution of $\Delta f = 0.70^\circ \text{C.}$ extirpated and suspended in the same medium, while the gills from the opposite side are filled with and suspended in Ringer's solution of $\Delta f = 0.50^\circ \text{C.}$

The measurements of oxygen consumption of such paired preparations in the respirometers gave uniformly consistent results. The gills in conditions designed to promote secretory activity always respired more, per gm. of tissue, than the gills in conditions designed to eliminate secretory

activity. The "secretory conditions" resulted in a rise of oxygen consumption of 30 to 80 per cent. above the "passive conditions." This difference was not found with other tissues of the eel studied in the same manner.

The generally high metabolism of the gill tissue is also notable—from two to five times as high as comparable respiratory rates for voluntary and involuntary muscles of the eel and the frog and about seven times as high as the rate for the whole intact eel. Comparison with mammalian lung shows that the gill tissue in the "secretory condition" has a relatively much higher oxygen consumption.

There is no direct proof that the high oxygen consumption of the gill tissue is causally related to secretory work, but the inferential argument is not negligible:

1. The conditions which are known to evoke secretory activity produce a very pronounced increase in oxygen consumption.
2. Similar conditions do not bring forth any such change in oxygen consumption in other tissues of the fish.
3. This enhanced oxygen consumption provides enough energy to satisfy at least 3 or 4 times the thermodynamic requirements for the secretion.

The fundamental processes involved in the secretion are not known any more than they are known for any secretory process. It seems reasonable to suggest, however, that this great question may be explored more advantageously with the relatively simple gills than with the more complex kidney.

Morphological Study of the Gill Membrane.

Essentially, the gill membrane comprises the barrier between the branchial blood and the external fluid in the very numerous tiny leaflets which project from the gill filaments.⁶ Each leaflet consists of a single fold of epithelium within which lies the system of blood channels. The fold of epithelium is kept open by a colonnade of "pilaster cells."¹⁵ These supporting cells are expanded at each end and these expansions, frequently fused together, form a base for the epithelial layer. Between the epithelium and the supporting cells there is evidence, at least in some cases, for the existence of a true basement membrane.^{6, 10, 18}

In most of the teleosts the limiting gill membrane consists primarily of a single layer of flat squamous epithelial cells, an exceedingly thin basement membrane, and the thin edges of the expanded ends of the supporting cells which form the blood channels. In *Amia calva* and in the toadfish (*Opsanus tau*) cuboidal and polyhedral cells make up the epithelium. In the sharks and rays the epithelium is composed of fairly thick polyhedral cells, usually interspersed with numerous mucous cells.

At the bases of the gill leaflets the membrane changes; squamous epithelium gives way, in part, to cuboidal and columnar cells, mucous cells become more numerous. In some species, notably the eel, there are large eosinophilic cells of glandular type which contain no mucous and which may represent a possible site for the chloride secretion.⁶ Bevelander¹⁰ suggests that these cells are merely inactive mucous cells;

¹⁵ Bietrix, E., *C.R. Soc. philomat.* (Paris), 1895, 8, 26. *Etude de quelques faits relatifs à la morphologie générale du système circulatoire à propos du réseau branchial des poissons.* Thèse méd., Paris.

¹⁸ Cf. Oppel, A., *Lehrbuch der vergleichenden mikroskopischen Anatomie der Wirbeltiere*, VI Teil, *Atmungsapparat.*, 1905, 76. Jena.

this seems doubtful in view of the marked histological difference in the cells and the fact that we have been unable to find transitional states between these cells and undoubted mucous cells except when poor fixation or staining technique was used.

Although it cannot be stated with certainty that the secretory activity in the branchial system is located in the gill leaflets, the arguments given on p. 978 make it probable that this is the site. In that case we have to admit that the cells responsible must be either the simple epithelium, the simple mucous cells, the supporting (endothelial) cells, or the cells described by Keys and Willmer.

We have made many measurements of the thickness of the gill membrane. With the exception of *Amia calva*, the toadfish (*Opsanus tau*) and the elasmobranchs, the gill membrane varied between 1 and 3 microns in thickness in the forty-five species investigated. While this is extremely thin, it is by no means so tenuous as the glomerular membrane of the kidney and is probably thicker than the epithelial layer in the alveolus of the human lung.

Estimates as to the extent of the gill membrane are of some interest. Lereboullet¹⁷ studied a lamprey (*Petromyzon marinus*) which had a body surface of about 0.08 sq. m., the estimated gill surface was 2.2 sq. m., or about twenty-seven times the body surface. This value is undoubtedly too high but more careful measurements by later workers are all in agreement as to the relatively large surface available for exchanges between blood and the external fluid.

Riess¹⁸ estimated a gill surface of between 810 and 925 sq. cm. in a pike weighing 650 gm. Pütter¹⁹ made a long series of measurements of the surface of the gill membrane. In different species he found values from 0.6 to 2.2 sq. cm. per gm. of total body weight. Pütter's values fit, within about ± 10 per cent., the equation:

$$\frac{S^{\frac{1}{2}}}{W^{\frac{1}{3}}} = C, \text{ where } S \text{ is the gill surface, } W \text{ is the body weight, and } C \text{ is}$$

a constant for any one species.

For the eel we have made independent estimates which agree, in general order of magnitude, with the values given by Pütter. Finally, we have calculated the surface of the gill membrane of the eel from the data given by Quekett²⁰ with similar results.

The exchange of the respiratory gases, oxygen and carbon dioxide, across the gill membrane cannot be discussed in any detail here. As in the lungs, the gas exchanges appear to be entirely passive and are dependent on the pressure or concentration gradients, the rate of ventilation of the branchial chamber and the rate of blood circulation. Winterstein²¹ found that from 20 to 70 per cent. of the total dissolved oxygen in the water was removed by a simple circulation past the gills of the fresh water fish, *Leuciscus*. The puffer fish, *Spheroides maculatus*, however, seems always to remove a constant amount, about 46 per cent., of the dissolved oxygen.²² There are no available data as to the absolute gas permeability of gill membranes.

I have found no consistent differences in the gill membranes of teleosts related to differences in oxygen requirements; increased need of oxygen is met primarily by an increased gill surface and not a change in the character of the surface (cf. also Keys,^{13a}). However, it may be noted that the

¹⁷ Lereboullet, A., *Anatomie comparée de l'appareil respiratoire*. Strasbourg, 1838.

¹⁸ Riess, J. A., *Arch. Naturgeschichte*, 1881, 47, Jahrg. Bd. 1, 518.

¹⁹ Pütter, A., *Die Ernährung der Wassertiere*, Jena, 1909.

²⁰ Quekett, J., *Trans. Micr. Soc. London*, 1847, 3, (1852), 1.

²¹ Winterstein, H., *Pflüger's Arch.*, 1908, 125, 73.

²² Hall, F. G., *Biol. Bull.*, 1931, 61, 457.

toadfish (*Opsanus tau*) which has an unusually thick gill membrane, is a fish of sluggish habits and very low metabolic rate.

Summary.

The requirements of salt and water economy in fishes force the conclusion that the gill membranes are relatively impermeable to water and crystalloids in spite of their large surface and extreme thinness.

The details of the branchial exchanges can be studied with considerable accuracy by various perfusion preparations. These membranes permit free exchange of carbon dioxide, oxygen, and ammonia and, except in the elasmobranchs, are relatively permeable to urea. There is a small but important water diffusion across the gill membrane and passive exchange of minute amounts of sodium and chloride can be demonstrated. The impermeability to crystalloids such as iodate, ferrocyanide, sulphate, calcium, glucose, etc., seems to be absolute.

The most remarkable property of the gill is its ability, in the marine teleosts, to perform secretory work of an order comparable to that of the mammalian kidney. There is an active transportation of NaCl in high concentration from the blood to the more concentrated sea water; the concentration of chloride or of sodium chloride automatically regulates this activity in a way which is independent of the total osmotic pressure, the total ionic strength and the sodium concentration.

Passive exchanges or equilibration cannot account for the secretion. An oxidative mechanism in the gill seems to provide the energy required for the secretion. The cells responsible cannot be localised with certainty but the choice falls primarily between the membranous epithelium itself, mucous cells, endothelial cells supporting the membrane, and the cells described by Keys and Willmer.

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GENERAL DISCUSSIONS.*

Mr. O. Gatty (Cambridge) said: The use of the term "polarisation-capacity" gives no clue to the origin of the phenomenon; this complicating factor can be eliminated by using constant polarising currents instead of alternating currents. Bowden and Butler and many other workers have used constant polarising currents on solution-metal interphases and have had considerable success in interpreting their observations, although solution-metal interphases show polarisation capacities with alternating currents. Electrical currents can produce chemical change; membranes cannot, therefore, be treated as an ohmic resistance in parallel with an electrical capacity. Moreover, overvoltage currents do not obey ohm's law; a logarithmic relation holds between current and potential difference. The factors so far discussed apply to interphases that can be considered to consist of one surface field; for mosaic membranes, at which local action currents can flow, other factors increase the difficulties in interpreting the membrane as an ohmic resistance in parallel with an electrical capacity; thus, the relative areas of two surface fields might be altered by electrolysis (as actually occurs with fields of metal oxide on metals during electrical polarisation). In biological systems, such other factors as concentration polarisation arising in very thin membranes, pore conduction, and of course variability of the material have to be considered. It is better therefore, to represent a membrane as an electrical

* On two preceding papers.

resistance in parallel with a capacity on which these factors are superposed. The resistance and capacity in parallel can be replaced by an equivalent circuit consisting of a resistance and capacity in series as suggested by Dr. Blinks, but in this case neither the resistance nor the capacity have so direct a physical relationship to the properties of the membrane.

The decrease in capacity as the eggs swell in dilute solutions is interesting as it would not be expected for the mere stretching of an elastic membrane; it follows that dilute solutions must effect the properties of the membrane itself. This conclusion is supported by observations on the charge of permeability constant with dilution obtained by several workers.

Professor A. Krogh (Copenhagen) (communicated): With regard to the postulated indifference of the fluid bathing the skin, I have found on fresh water fishes that the skin is, at least in several forms (trout, carp) relatively more permeable to salt and water than the gills, but the gills are much more liable to damage by an unfamiliar environment. Homer Smith observed a very low permeability for urea and ammonia in the skin, but a fairly high for chlorine. I see no reason to doubt Schlieper's result that the Cl secretion through the gills takes place without water, and I can confirm the result for frogs and other fresh-water forms. Schlieper observed a definite increase in Cl secretion when the osmotic pressure of the perfusion fluid was raised by glucose or sulphate. The mechanism by which secretion is activated will require much further study.

Professor H. Freundlich (London) said: In living organisms true equilibria appear to me extremely improbable; we ought to consider, mainly, stationary states and reaction processes. Obviously, there is an essential difference between a true equilibrium and a stationary state; phenomena in a jet of liquid differ from those of the state of equilibrium in a liquid mass not only in order of magnitude, but also in kind. Like living matter, a stationary state may show "irritability," i.e., a small change from without may cause large changes in a stationary state; on the other hand, it is distinctive of a true equilibrium that it responds with a small change to a small change from without.

A seemingly anomalous distribution of a solute (transport of a substance against its concentration gradient or in the absence of such a gradient) may be brought about, when diffusion of some other substance proceeds or when a stationary state of a concentration gradient is maintained. If, for instance, a gradient in the composition of substances B, C, etc., is maintained in a column of a solution containing a substance A in uniform distribution, A may be made to diffuse and to assume an unequal distribution, so long as there is a gradient.¹ Hence, even though a final state of equilibrium is reached at which all substances are uniformly distributed the path to this state is simple and straightforward. Such anomalous diffusion is not connected with the interaction of electrolytes;² it occurs also when one of the substances is an electrolyte and the other a non-electrolyte, or when both are non-electrolytes. The diffusion pressure acting here is not simply identical with the osmotic pressure; it is also correlated with the "solubility" of the solutes, in a very general sense of this term.

¹ *Diffusion retrograde of Thoevert (Ann. chim. et physique, 1902 (7), 26, 419; Ann. physique, 1914 (9), 2, 405); cf. further G. S. Hartley (Trans. Faraday Soc., 1931, 27, 10; also ibid., 1931, 27, 1), and Teorell, Proc. National Acad. Scienc., 1935, 21, 152.*

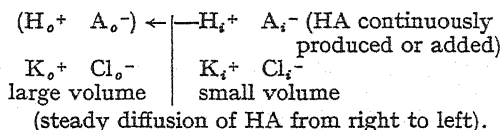
² A closely related phenomenon, which is apparently bound to the diffusion of electrolytes through membranes which are not strictly semipermeable, is anomalous osmosis, where liquid is transported from the more concentrated solution to the more dilute one. Anomalous osmosis seems to be mostly due to electrosmosis caused by membrane potentials (Söllner and Grollman, *Z. Elektrochem.*, 1932, 38, 274; *Trans. Electrochem. Soc.*, 1932, 61, 477.

These phenomena have not been investigated thoroughly. It would be interesting to know, whether Na⁺- and K⁺-ion behave very differently, when influenced by the concentration gradient of other substances; ³ this is to be expected.

I do not imply that abnormal distribution of substances in living matter is entirely due to anomalous diffusion, nor do I wish to discuss details of the mechanisms which may play a rôle; but since conditions in living matter are most favourable to anomalous diffusion, one ought to test how far the latter may be instrumental in causing an anomalous distribution of substances.

Dr. T. Teorell (*Uppsala*) said: I have already pointed out that the electrical potential gradients in living systems can perform work against concentration gradients (*cf.* pp. 920 and 940). The Donnan equilibrium furnishes the simplest artificial system in which ions can migrate "up-hill" owing to electrostatic effects. The characteristic feature in Donnan systems is the presence of one or more *non*-diffusing constituents and a perfect equilibrium in a thermodynamical sense. When dealing with living matter, however, the typical property is lack of true equilibria. Instead we have to deal with "dynamical machinery." Biological systems are in general in a steady state; it is essential, therefore, to develop theories for simple dynamical systems. An attempt in this direction was made recently.⁴ A theory was presented for the "diffusion effect" on ionic distribution, the chief points of which were:

Consider a convection-proof boundary (for instance a membrane) separating a large volume of KCl solution from a small volume into which a continuous addition of HA is made, so as to maintain a constant concentration gradient of either H or A:



In this system *all* constituents are freely diffusible across the membrane. Due to a difference in mobility of the ions of the "diffusing agent," u_H and v_{Cl} , an electrical potential gradient will be set up within the membrane ($u_H > v_{Cl}$). This will cause the K to migrate inwards to the cell and the Cl to migrate outwards. The redistribution of the "passive ions," K and Cl, will continue until a final steady state is produced, when the "osmotic" gradients which are built up will balance the electrical gradients.⁵ The theory predicts that the ionic distribution in the steady state is characterised by the expression $K_i/K_o = Cl_o/Cl_i$, which is immediately recognised as being valid also for the Donnan effect. In fact, the Donnan equilibrium can be regarded as a limiting case in this theory, which is obtained when the mobility, within the membrane, of either H or Cl approaches zero. The distribution ratio is

$$\log \frac{K_i}{K_o} = \frac{u_H - v_{Cl}}{u_H + v_{Cl}} \log \frac{H_i + K_i}{H_o + K_o}.$$

An alternative formula in terms of the membrane potential in the steady state is (π = millivolts):

$$\log \frac{K_i}{K_o} = \frac{\pi}{58}.$$

The predicted "diffusion effect" on the ionic distribution has been experimentally confirmed in simple electrolyte systems.⁶ Protein and

³ An experiment by Thovert (*Ann. chim. et physique* ¹, with NaCl and KCl and a concentration gradient of HCl shows a distinct difference between Na⁺- and K⁺-ions, but is perhaps not quite conclusive.

⁴ *Proc. Nat. Acad. Sci.*, Wash., 1935, **21**, 152.

⁵ See page 939.

⁶ *J. Gen. Physiol.*, 1937, *in press*.

colloids can easily be subjected to the influence of a steady diffusion of some other component in the system.⁷ In the latter cases the redistribution results may be very marked even in the presence of a comparatively small membrane potential, because of the high valency or charge carried by the protein or colloid particles. These effects must not be confused with electrophoresis, because no current is flowing. The whole phenomenon of the "diffusion effect" on the ion or micelle distribution is due to exchanges between ions or charges resulting from differences in mobilities and concentrations. Finally, it should be pointed out that the system, considered as a whole, is "dynamical machinery" of a type, which may well have biological analogies: a steady diffusion of one substance, requiring energy for its maintenance, causes accumulation or impoverishment of other substances.

Professor Ancel Keys (*Rochester, Minn.*), in reply, said: Smith's observations on the permeability of the skin of the fish leave several questions unsettled. In the first place, the rôle of the deposition of guanidine and other nitrogenous residues in the skin and in the scales must be evaluated in order to get a correct measure of the permeation of these structures by urea and ammonia. If, as has been suggested by others, the formation of guanidine takes place *in situ* and urea and ammonia are the nitrogen sources for this guanidine, true estimates of permeability of the skin to these substances from either inside or outside will require more elaborate precautions than have been taken heretofore. Without such precautions one should expect that permeability to urea from inside out might be underestimated if the appearance of urea in the outer medium is taken as the criterion. On the other hand, if disappearance of urea from the outer medium is the criterion for estimating the permeability in experiments where the external medium has a high urea content, then the permeability might easily be grossly overestimated.

Somewhat similar arguments might be made about estimates as to the permeability of the skin to chloride in view of the fact that in many animal forms the skin appears to exercise a marked reservoir function for chloride.

In any case it does not seem possible, without additional evidence, to compare such diverse structures as the skin of the elasmobranch fishes, the skin of the frog, and the smooth and scaly types of teleost skins. Not only are these skins structurally different, but the differences in salt, water and urea economy in these several animal forms may well be associated with functional differences in their skins.

The exchange of Cl in a system where little or no thermodynamic work is required is, at least so far as physical chemistry goes, vastly different from an exchange requiring the performance of large amounts of thermodynamic work. The fundamental biological mechanism may, actually, be the same in both instances—though there is no compelling reason to think so—but even if this is the case, the operation of the mechanism may be quite different. Accordingly, it would seem rash to accept Schlieper's experiments as anything more than suggestive of interesting possibilities. In my opinion, the distinction between exchanges resulting in a marked increase in the free energy of the system and relatively passive exchanges must be given the greatest emphasis.

Schlieper's few observations provide a slender basis for concluding that osmotic pressure is the primary force which activates the gill secretion. There is no doubt that, even if the secretion can be stimulated by glucose or sulphate, the activation by chloride is much more powerful. I thoroughly agree, however, that the mechanism of the activation of the secretion will require much further study.

Professor K. C. Cole's reply, if received before going to press will be inserted at the end of this number.

⁷ Cf. remarks on pp. 940 and 1141.

THE PERMEABILITY OF PLANT PROTOPLASTS TO NON-ELECTROLYTES.

By RUNAR COLLANDER.

Received 23rd February, 1937.

Our knowledge of the permeability of plant protoplasts to non-electrolytes has increased with remarkable rapidity during the last ten years. Although in the nineties Ernst Overton, the founder of the modern study of protoplasmic permeability, carefully investigated the permeability of a very large number of different plant and animal cells to a variety of non-electrolytes as well as of electrolytes, his projected great publication on protoplasmic permeability was unfortunately never completed. We therefore know his results, especially as far as plant cells are concerned, only from some short papers¹ which, although the main results are excellently summarised, contain only scanty concrete facts. The first plant objects of which the permeability was the subject of detailed papers were the bacterium *Beggiatoa mirabilis* studied in 1925 by Ruhland and Hoffmann² and later by Schönfelder,³ and the epidermal cells of *Rhoeo discolor* studied in 1929 by Bärlund.⁴ Since then the progress in this field has been very rapid, so that at present more than thirty very different kinds of plant cells have been fairly closely studied with regard to their permeability to various non-electrolytes.⁵

In this paper we shall first consider more closely the permeability properties of one particular object and then compare with each other the different objects hitherto studied.

As the standard object to be treated more in detail we choose the large, multinucleate cells of an alga, viz. *Chara ceratophylla*.⁶ This object is so far the only one the permeability of which to non-electrolytes has been closely studied, using a direct method of work, i.e., by analysing quantitatively the cell sap squeezed out from single cells which have been placed for known time intervals in solutions of the substances to be studied. Obviously such a method of permeability measurement involves a minimum of theoretical assumptions, whereas the method most widely used, viz. the plasmolytic method, is theoretically open to several objections, though it also seems to give quite useful results in the hands of a skilful worker.

All experimental facts seem to indicate that the penetration of the *Chara* cells by dissolved non-electrolytes is a simple diffusion process in which the only significant concentration gradient in most cases is that

¹ Overton, E., *Vierteljahrsschr. Naturforsch. Ges. Zürich*, 1895, 40, 159; 1896, 41, 383; 1899, 44, 88.

² Ruhland, W., and C. Hoffmann, *Planta*, 1925, 1, 1.

³ Schönfelder, S., *ibid.*, 1930, 12, 414.

⁴ Bärlund, H., *Acta Bot. Fennica*, 1929, 5, 1.

⁵ The two most recent comprehensive publications in this field are: Hofmeister, L., *Bibliotheca Bot.*, 1935, 113, 1, and Marklund, G., *Acta Bot. Fennica*, 1936, 18, 1.

⁶ Collander, R., *ibid.*, 1930, 6, 1; Collander, R., and H. Bärlund, *ibid.*, 1933, 11, 1.

across the protoplasm itself. Thus Fick's law is directly applicable in the following form:

$$P = \frac{v}{qt} \ln \frac{C}{C - c},$$

where v is the volume (cm^3) and q the surface of the cell (cm^2), c the internal concentration of the penetrating substance at the time t , C its equilibrium internal concentration (almost identical with its external

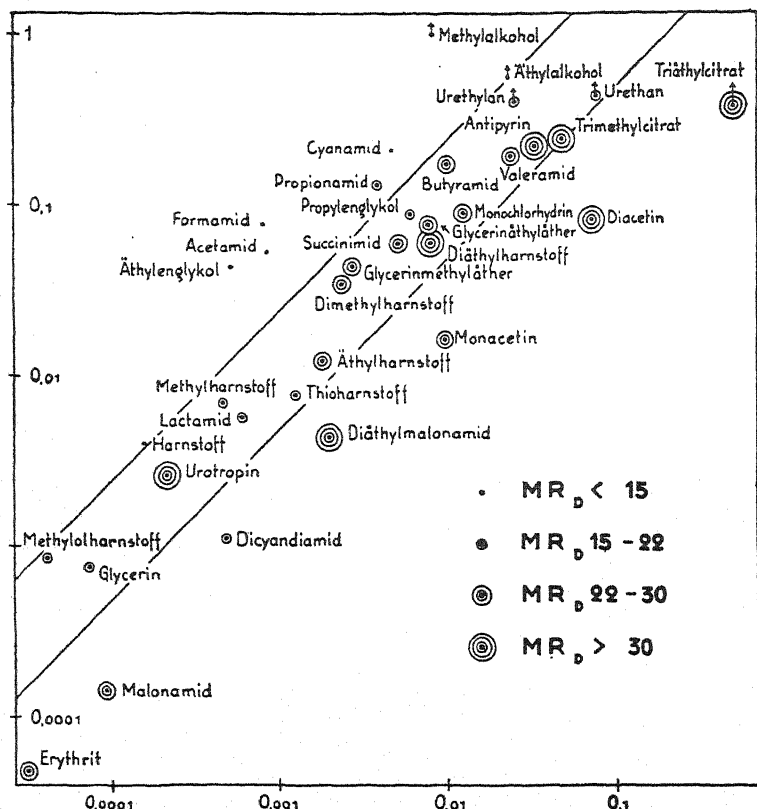


FIG. 1.—Permeability of the cells of *Chara ceratophylla* to various non-electrolytes. Ordinates indicate the permeability constants (cm^2/hours). The abscissa gives the oil/water distribution coefficients of the substances studied. After Collander and Bärlund (somewhat changed).

concentration), and P a constant which measures permeability and which is therefore termed the permeability constant.

To test the validity of the current hypotheses concerning protoplasmic permeability, viz. (1) the lipid-solubility hypothesis, (2) the ultrafiltration hypothesis, and (3) a combination of these, i.e., the lipid-sieve hypothesis, measurements were made of the permeability of the *Chara* cells to 45 organic non-electrolytes of very different lipid solubility and different molecular size. In addition, the distribution of all these substances between ethyl ether and water, as well as between olive oil and water was determined so that it is possible to use the dis-

tribution coefficients thus obtained as a provisional measure of their relative lipid-solubility. As a measure of their molecular volume the molar refraction (MR_D) can be used. The result of this study is represented in Fig. 1 from which, however, those substances are omitted which either penetrate the *Chara* cells so slowly that their permeability constants could not be determined or the oil-solubility of which is so slight that it could not be determined experimentally. To some substances the protoplasm is so permeable that they could probably permeate faster, were it not for the comparatively slow diffusion through the cell sap; such cases are indicated by upwardly directed arrows.

There is clearly a somewhat close correlation between the oil-solubility of the substances on the one hand, and their permeability constants, on the other; this is not merely a general concordance but, at least approximately, a direct proportionality. This is shown by the fact that most of the points in Fig. 1 fall between the two parallel lines cutting the axes at an angle of 45° . On the other hand, the smallest molecules obviously permeate faster than would be expected on account of their oil-solubility alone.

We thus see that both the lipid-solubility and the molecular volume (or some other properties varying in close accordance with these) are factors involved in the permeation process. It seems, therefore, natural to conclude that the plasma membranes of the *Chara* cells contain lipids, the solvent power of which is on the whole similar to that of the olive oil. But, while the medium-sized and large molecules penetrate the plasma membrane only when dissolved in the lipids, the smallest molecules can also penetrate it in some other way. Thus, the plasma membrane seems to act both as a selective solvent and as a molecular sieve.

Against this view, for which the name "lipid-sieve hypothesis" has been proposed,⁷ at least three objections have been raised:

(1) Some authors⁸ are of the opinion that it is not necessary to assume the occurrence of lipids in the plasma membrane as, for example, hydrophobic proteins also would favour the passage of lipid-soluble, i.e., hydrophobic solutes through the membrane. However, so far as the present writer is aware, there has never been observed a preferential permeability of pure protein membranes to lipid-soluble substances which would be even remotely similar to that of the living protoplasts. So far it seems, therefore, most reasonable to ascribe the favoured permeation of lipid-soluble substances through the protoplasm to the occurrence of some sort of lipids in the plasma membranes.

(2) Provided that the plasma membrane contains lipids as an essential component, it does not necessarily follow that the lipid-soluble substances must penetrate the membrane truly dissolved in the lipids. It is well known that lipid-soluble substances are in most cases also surface-active and their great penetration power might therefore perhaps be ascribed, not so much to their solubility in lipids, as to their adsorption at the water/lipoid interfaces and, it may be difficult, and perhaps even unwise, to distinguish very sharply between these two effects. If the plasma membrane is only a few molecules thick and consists of strongly oriented molecules, then evidently such expressions as "solubility in the plasma membrane substances" or "adsorbability

⁷ Poijärvi, L. A. P., *Acta Bot. Fennica*, 1928, 4, 1.

⁸ Brooks, S. C., *Arch. exper. Zellforsch.*, 1934, 15, 236; Frey-Wyssling, A., *Die Stoffausscheidung der höheren Pflanzen*, Berlin, 1935.

by the lipid particles of the plasma membrane" must clearly be only very cautiously used. Nevertheless, the observed proportionality between oil-solubility and penetration power seems to make it preferable to interpret the relations between the physico-chemical character and the penetrating power of different substances in terms of solubility rather than in those of adsorption.

(3) Finally, it has been suggested⁹ that the faster penetration of the smallest molecules may be due simply to the well-known fact that the diffusibility of dissolved substances always (*i.e.*, when there is free diffusion) decreases with increasing molecular size. This suggestion does not necessarily involve the assumption of a special sieve-effect in the case of protoplasmic permeability; it, however, disregards the fact that the rate of free diffusion decreases rather slowly with increasing molecular size, while the penetrating power often decreases fairly abruptly when the MR_D increases, for example from 10 to 20.

We thus reach the conclusion that among the permeability hypotheses so far put forth the lipid-sieve hypothesis seems best to explain the permeability of the *Chara* cells to non-electrolytes. Let us now turn to the permeability of other plant cells.

Fig. 2 gives an idea of the permeability of the sixteen plant objects so far studied in this laboratory.¹⁰ Each object is represented by a vertical line on which the permeability constants of seven substances are denoted by points using a logarithmic scale. The objects are arranged according to increasing permeability to erythritol.

It should be noted that the sixteen objects in Fig. 2 represent extremely different types of plant cells. Thus, such very different taxonomical groups as flowering plants, mosses, green algae, diatoms, brown algae, red algae, blue-green algae and bacteria are represented. Also the physiological character of the cells examined varies greatly. Nevertheless, all these cells agree in the main features of their permeability. If the lipid-sieve hypothesis is accepted as an explanation for the permeability of the *Chara* cells, then it seems logical to accept it also in the case of the other objects.

This impression is even strengthened by a closer examination of the permeability differences, admittedly very great, between some of the objects studied, for it is easy to show that these differences are, at least for the most part, such as could be predicted from the standpoint of the lipid-sieve hypothesis. Some examples will make this clear. (1) *Spirogyra* and *Chara* are seen from Fig. 2 to agree very closely as to their permeability, except that the permeability of the *Chara* cells is about three to ten times greater than that of *Spirogyra* cells. Obviously such a difference can, at least theoretically, be explained on the assumption that the plasma membrane of *Spirogyra* is correspondingly thicker than that of *Chara*. (2) The epidermal cells of *Rhoeo* have an exceptionally low permeability to all amides. (Thus *Rhoeo* is unique among the sixteen objects in being less permeable to malonamide than to erythritol and also in being less permeable to methyl urea than to glycerol.) This peculiarity can easily be explained along lines first put forth by Höber and his school.¹¹ It can be shown experimentally that the addition of an oil-soluble acid to a neutral oil largely increases its

⁹ Traube, I., and F. Dannenberg, *Biochem. Z.*, 1928, 198, 209.

¹⁰ Except objects studied by Bärland,⁴ Collander and Bärland,⁶ and Marklund,⁵ Fig. 2 also comprises some hitherto unpublished results of Mr. J. E. Elo.

¹¹ Höber, R., *Biol. Bull.*, 1930, 58, 1; Wilbrandt, W., *Pflüger's Arch.*, 1931, 229, 86.

solvent capacity for amides. This being known, we have only to assume that the plasma membrane lipoids of most plant cells are more or less acidic in character while those of *Rhoeo* are approximately neutral. (3) The root cells of *Lemna* differ from most other plant cells in being more permeable to urea than to the more lipoid-soluble methyl urea. Perhaps this can be explained on the assumption that the plasma membrane of the cells in question contains a considerable number of pores of such a diameter as to be just penetrable by the urea molecules but not by the somewhat greater molecules of methyl urea. (4) The two diatoms so far studied, viz. *Melosira* and *Licmophora*, are both characterised

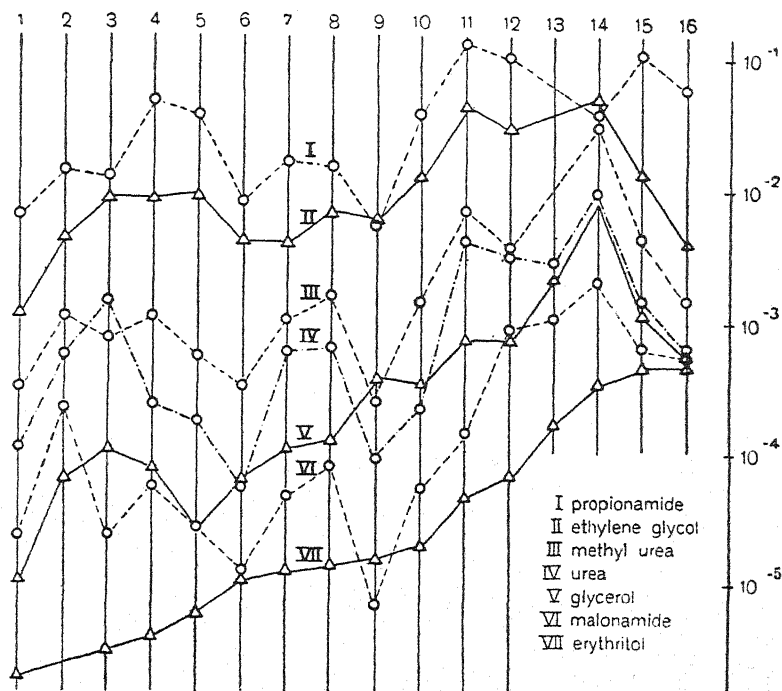


FIG. 2.—Permeability of sixteen different kinds of plant cells to some non-electrolytes: 1. Leaf cells of *Plagiothecium denticulatum*, 2. *Oedogonium* sp., 3. root cells of *Lemna minor*, 4. *Pylaiella littoralis*, 5. *Zygnema cyanosporum*, 6. subepidermal cells of *Curcuma rubricaulis*, 7. *Spirogyra* sp., 8. leaf cells of *Elodea densa*, 9. epidermal cells of *Rhoeo discolor*, 10. epidermal cells of *Taraxacum pectinatifolium*, 11. "leaf" cells of *Chara ceratophylla*, 12. internodal cells of *Ceramium diaphanum*, 13. *Bacterium paracoli*, 14. *Oscillatoria princeps*, 15. *Melosira* sp., 16. *Licmophora* sp.

by their remarkably high permeability to erythritol and sucrose, i.e., to substances which have an extremely low lipid-solubility and a considerable molecular volume. This fact points to the occurrence of plasma membrane pores of an extreme width in these cells. (5) A great abundance of somewhat smaller plasma membrane pores may be assumed in the case of *Oscillatoria* which differs from most other cells in that the sieve principle is more dominant and the effect of the lipid-solubility less so than in other cases. (6) When *Chara* cells are placed in a glycerol solution it takes about two days before the glycerol concentration in the interior of the cell reaches one-half* of its concentration in the

external solution. With the cells of *Bacterium paracoli*, however, the same state is reached in less than a minute. The first impression is, of course, that the permeability of the bacterial cells is of quite a different order of magnitude than that of the *Chara* cells. This impression is however erroneous, for if the permeability is expressed, as in Fig. 2, per unit cell area it is found that there is in reality only a rather slight permeability difference between *Chara* and the bacterium.

It is not possible to present here in detail the results of the numerous permeability measurements carried out in other laboratories. Suffice it to say that the results are, for the most part, easily explicable in terms of the lipid-sieve hypothesis. This applies even to that object, viz., *Beggiatoa mirabilis*, which, among all plant cells so far studied, deviates most strikingly from the main type. While in most plant cells the lipid-solubility is the factor primarily responsible for the different permeation capacity of different solutes, their molecular volume being a factor of minor importance, just the reverse is true in the case of *Beggiatoa*. It is however, interesting to note that *Beggiatoa* has not a completely isolated position in regard to its permeability, for *Oscillatoria* forms an obvious connecting link in this respect between *Beggiatoa* on the one side and most plant cells on the other.

It still remains to consider the question what kind of structure would best explain the permeability qualities of the plasma membrane.

The rather strongly accelerated penetration of the smallest molecules makes the existence of a homogeneous lipid layer consisting of random oriented molecules unlikely. It seems, on the contrary, that some sort of a sieve-like structure must be attributed to the plasma membrane. Perhaps the simplest assumption of this kind is that the plasma membrane consists of a few layers of regularly oriented lipid molecules. The plasma membrane would thus have a structure like that of the phosphatide double films recently described by Bungenberg de Jong and Bonner¹² or like the oil films invented by Danielli.¹³ Unfortunately, almost nothing seems to be known at present about the permeability properties of such films, but from a purely theoretical point of view it seems probable that they will show a preferential permeability (a) to lipid-soluble substances and (b) to extremely small molecules, thus corresponding at least in a general way to the demands of the lipid-sieve hypothesis. It is very much to be hoped that the permeability properties of these artificial films should be cleared up as soon as possible. Perhaps it will then turn out that some of these films correspond in their permeability so closely to the plasma membrane that an essential conformity, also in structure, must be assumed to exist between them.

Finally, it should perhaps be pointed out that the present writer is quite aware of the fact that not only electrolytes but probably also non-electrolytes may often be actively absorbed or excreted by living cells, the simple laws of diffusion being not directly applicable to such cases. For this active transport of matter Overton, already in the nineties, proposed the term "adenoid activity." It seems in fact important to distinguish carefully between this activity on the one side and the simple permeability processes on the other, for they probably have very little in common.

University of Helsingfors.

¹² Bungenberg de Jong, H. G., and J. Bonner, *Protoplasma*, 1935, 24, 198.

¹³ Danielli, J. F., *J. Cell. Comp. Physiol.*, 1936, 7, 393.

ELECTRICAL EVIDENCE ON THE NATURE AND ALTERATIONS OF MEMBRANES IN LARGE PLANT CELLS.

By L. R. BLINKS.

Received 2nd March, 1937.

Materials and Methods.—The organisms here reported upon are very large plant cells, with extensive, uninterrupted living ("protoplasmic") layers, only some 10 microns or so thick, but spread out over surfaces often several square centimetres in area, surrounding a large central cavity ("vacuole"), 0.1 c.c. to 25 c.c. or more in volume. The latter is filled with the "cell-sap," which can be readily extracted, with little or no alteration. In most cases it is largely an inorganic salt solution, often rich in KCl, and notably lacking in organic matter. In one cell (*Halicystis*), this cell-sap can be replaced, through two fine perfusion tubes, with any desired new solution, with characteristic electrical results. The cells are either long and cylindrical (as in *Nitella*), or cylindroid to spherical (in *Valonia* and *Halicystis*); in the former it is easier to employ two external contacts on definite measured surfaces, for electrical leads; in the latter two cells, fine glass tubes can be inserted across the protoplasmic film, making a direct salt-bridge connection to the vacuolar sap. Proper KCl-agar salt bridges complete the circuits to calomel half-cells, which are connected to the electrometer or bridge circuit employed.*

Resistance.—One of the oldest and best evidences that some sort of membrane is probably present on living protoplasm is the hindrance it offers to the passage of electric current. Whether Faraday himself studied this I do not know, but it must have been realised soon after his first electrolytic studies. Some change occurs on death or injury which greatly decreases the resistance—in some cases as much as 90 per cent. (e.g. in Osterhout's measurements with *Laminaria*). However, the resistance is usually called "high," and most of its measurements have been necessarily relative, rather than absolute, since the shunt resistance around the cells in most tissues is uncertain.

By taking advantage of the large size of *Valonia* and *Nitella* cells, I was able several years ago to estimate fairly closely the shunting resistance. (The method involved removing protoplasm and sap, and inflation of the cell-wall, in nearly normal moisture and salt content, for direct measurement.) By comparison with the original living resistance it was possible to calculate what had been the effective resistance of the protoplasm itself (to direct current).

In *Nitella* (fresh water plant) this had the surprisingly high value of 100,000 to 700,000 ohms per sq. cm. of protoplasmic surface, with a fair average value of 250,000 ohms./cm.² In *Valonia* (marine plant), it ran

* For details of technique, and for actual string galvanometer records documenting these verbal descriptions, the reader is referred to the following papers in the *J. Gen. Physiology*, 1929-30, 13, 361, 495, 793; 1930-31, 14, 139; 1932-33, 16, 147; 1933-34, 17, 109; 1934-35, 18, 409; 1935-36, 19, 633, 673, 867; 1936-37, 20, 229.

as high as 50,000 ohms/cm.², with an average of 10,000 ohms/cm.². Since another fresh water plant agrees well with *Nitella*, and another marine one with *Valonia*, we may assume that the lower values for the latter may be due to the greater salt content of the protoplasm.

While these are far from perfect insulators, the actual specific resistance of the membrane material may be fairly high, considering its probable thinness. Evidently there is not very much continued ionic transfer under the conditions of measurement; this is consistent with the maintenance of large differences in ionic concentrations between cell sap and the outside fluids, perhaps most marked for K⁺ and H⁺ ions, where gradients of 50 to 100 fold are maintained through the life of the cell.

Although the passage of continued current is slight, much greater currents pass the protoplasm under special conditions. One of these is purely physical, resulting from the capacity of the membrane; the other is subject to chemical and biological control, and probably involves alteration in the membrane itself.

Transient Phenomena; A.C. Impedance.—At the moment of applying an E.M.F., much larger currents pass the cell than later, when a steady state is established. If the bridge is balanced to the continuous current resistance values mentioned in the preceding section, a quick detector (*e.g.*, Einthoven string galvanometer with proper amplifier) shows a marked deflection away from the zero or base line at "make." It then approaches zero again in a regular curve occupying from one or two tenths of a second up to a second or more in some cases. No further change occurs during current flow, but at "break" a deflection occurs in the opposite direction and dies away in a regular curve nearly the mirror image of that at make. A counter-E.M.F. has appeared in the cell, opposing the applied E.M.F., causing the large initial current to decrease, and producing the momentary current in the opposite direction on its discharge.

This counter-E.M.F. always accompanies and largely accounts for the high apparent resistance of the living cell. No such deflections occur in a dead cell balanced to its low steady state resistance (essentially that of its cell sap). Furthermore, if a living cell is balanced against this "dead" value, no deflection now occurs at the instant of make, since the instantaneous current is such as would be expected from the ohmic resistance of the dead cell. Then as the counter-E.M.F. builds up, the detector image moves away from zero and reaches a constant deflection which is maintained as long as the reduced current flows. At break it returns in another regular curve to the base line.

The greater current flow at make, and the appearance of counter-E.M.F., of course represents a capacity effect, which is quite large—up to 1 μ F per sq. cm. of cell surface. This large capacity also causes the impedance to vary with the frequency of alternating current used to measure it. In these cells, contrary to the situation in many cell suspensions or tissues, the impedance is very much lower at 1000 cycles than in D.C., and is very sensitive to frequency changes. It falls rapidly over the range 0 to 10,000 cycles, above which it is very low, constant and essentially that of a dead cell (due to the cell sap alone).

Nature of the Capacity (Polarisation or Static?)—Both of the effects mentioned (D.C. transients and impedance changes in A.C.) might be due to a static capacity, such as would result from a very thin dielectric film or membrane. This simplest hypothesis appears to fail

in several respects. The charge and discharge of a static condenser follows an exponential time course; the transient curves with cells only roughly approximate this, as shown by their residual D.C. deviations when balanced against a static condenser in the bridge. The time constant of a condenser is also lengthened by an increased resistance inserted in series; the transients in *Valonia* at least are remarkably independent of such external changes of resistance. Finally, to maintain bridge balance by means of a series-parallel circuit representing the elements of the cell (protoplasm in series with sap, both shunted by cell wall), the capacity setting is not constant, but decreases with increasing frequency of alternating current. An associated series resistance also decreases, nearly inversely with frequency. While somewhat similar spurious effects can result from purely static capacity distributed along cells or under the contact surfaces (as in a cable), they still persist to some extent when distributed capacity is greatly reduced, or entirely obviated (as in impaled cells).

Very similar deviations from exponential time course, independence of external circuit, and changes of capacity with frequency, characterise polarising electrodes. It is therefore suggested that protoplasm (in *Valonia*) displays some polarisation capacity, possibly in parallel with a purely static component, since both the actual capacity and its changes are less than at a platinum electrode in KCl. This is consistent with the fact that living cells are very permeable to undissociated, lipoid soluble molecules, but also display some differential permeability to ions, e.g., K^+ and Cl^- (see below). However, we need to know much more about polarisation phenomena in artificial membranes or at phase boundaries before the biological capacity effects can be interpreted.

Directional Effects.—In the case of cells with 2 external contacts, the base line during current flow is, of course, essentially zero, since any constant potentials at each end of the cell cancel each other. Similarly, the curves of counter-E.M.F. are due to changes at each contact, one with current flowing inward across the protoplasm, the other outward. The resultant is an average effect, which misses any directional characteristics. Fortunately in these large plant cells it is possible to study the latter as well.

This may be done either by killing or altering one contact area, with loss of its potential and polarisation characteristics while leaving the other for some time intact; or by inserting a fine glass tube through the protoplasm and into contact with the sap (impalement).

It is found that many of the effects remain the same as above described. Counter E.M.F.'s develop against moderate currents in either direction, and are about proportional to the current density. If the latter is increased up to fairly high values, for inward current, a point is reached where no greater counter E.M.F. develops for any increase of current, and there may even be a recession, giving a cusped rather than asymptotic time course. The highest increments so produced may be 100 to 200 mv., or to a total of 300 mv. maximum P.D. Considering the probable thinness of the protoplasmic membrane, this is rather high electrical stress. However, the membrane is apparently still "elastic," and recovers to a normal P.D. and regular subsequent polarisation after each strain.

Stimulation, or Reversal of P.D., by Outward Current.—Outward current may have much greater effects, however. In *Valonia*, with a normally negative P.D. (outside of protoplasm negative to the

measuring instrument), recessions from polarisation may begin at much lower current densities passing outward across the protoplasm, and the membrane may take appreciable time to recover after large flows. The strain is more lasting and takes longer to repair.

In *Nitella* and *Halicystis*, with normal positive P.D., still more striking results occur. Up to a threshold of outward current (much lower in *Nitella* than *Halicystis*) only a regular decrease of P.D. results, with recovery at break of current. At this threshold, however, the polarisation curve inflects, assumes a sigmoid course, and the cell undergoes a very rapid decrease of positive P.D., to about zero in *Nitella*, or to actual negative values in *Halicystis*. There are other differences in the two cells: this "stimulation" once initiated in *Nitella* to a certain point, goes on to completion even if the current ceases to flow, while in *Halicystis* the P.D. remains reversed only while the current flows. *Nitella* also shows an independent, spontaneous recovery *even though the stimulating current continues to flow in undiminished density*; *Halicystis* only recovers positive P.D. when the outward current flow is stopped.

If rapid makes and breaks, say of $\frac{1}{2}$ to 1 second duration, are made during the "stimulation" course of *Nitella*, another remarkable change is found; at the height of stimulation, when the P.D. has dropped nearly or quite to zero, it is found that all polarisation responses are also gone; no counter-E.M.F. develops to either inward or outward current of a density which evoked it before stimulation. It is strongly suggested that a membrane has actually been destroyed, or so altered as to lose its vital electrical characteristics (both P.D. and polarisability), and to become momentarily a strictly ohmic, non-reactive conductor of low or negligible resistance. The normal P.D. and capacitative reactance then reappear together as recovery proceeds.

This remarkable lability is of more than special interest, for it seems to be the essential protoplasmic property utilised in transmissions of stimuli. Thus the alteration initiated at one point by outward current flow in *Nitella*, soon appears farther down the cell, travelling at a rate of 1 or 2 cm. per second. It seems quite certain that the original stimulated spot, in losing its P.D., becomes the sink into which nearby positive sources can discharge; the flow of current outward across these stimulates them in turn, they lose their potential, and the disturbance spreads down the cell in a series of such closed local circuits. One cell can even stimulate another entirely separate cell if proper salt bridges are supplied to give a completed circuit.

Since such a mechanism is also widely accepted to account for nerve transmission, it is obvious that breakdown and repair of the protoplasmic membrane is an important process. Owing to the slowness of the cycle in *Nitella*, much more can be learned of its characteristics than in nerve. *Halicystis*, being still slower, and showing no spontaneous recovery during outward current flow, has also contributed to the analysis.

Here the situation is still simpler, for only one surface of the protoplasm (probably the outer) appears to be altered or destroyed. Evidence points toward the existence of two discrete potentials, one positive and one negative, whose summation gives the total 70 to 80 mv. outwardly directed potential normally observed. One of these, the positive potential, is quite labile, being destroyed by alterations in the salt ratios of sea-water; by internal p_H changes produced either directly by perfusion or indirectly by the penetration of ammonia; and finally, by the

flow of outward current. All these treatments still leave a large negative P.D. of 40 to 60 mv.; and polarisability is even more prompt and marked than it is normally. One membrane, probably that at the vacuolar surface, is apparently still intact (other, visual evidence in many cells indicates that this membrane, the "tonoplast" of de Vries, is very resistant, and persists even after the destruction or dissolution of the rest of the cell).

Particular emphasis is placed upon the similarity of current flow effects to those produced by dilute ammonia added to the sea-water. These not only duplicate each other almost exactly in the negative values reached, and in the shape of the time curves (differing only in actual speed); but in the existence of thresholds, and the actual lowering of these for one treatment by the other. Thus a much lower current density causes reversal of P.D. in *Halicystis* treated with subthreshold ammonia (itself insufficient to reverse). A very remarkable hysteresis is often shown at just sub-threshold ammonia concentrations; here a reversal is effected by an extremely small outward current, and at the break of current the P.D. remains permanently reversed. Only on passage of a small *inward* current is positive P.D. regained. This metastable state, in which a small added stimulus can destroy or reform a membrane resembles the "all-or-none" response to stimulus in *Nitella*. Spontaneous recovery of positive P.D. does not then occur in *Halicystis*, but the experimental conditions preclude the return flow of inward current, from neighbouring regions, which may assist the recovery in *Nitella*.

Since ammonia definitely increases the p_H of the sap, and its effects can be duplicated by perfusion or more alkaline solutions in the vacuole, it may well be that current flow likewise produces its similar effects through an increased p_H at some critical surface—possibly by saponification or emulsification of a continuous lipoid phase. While direct evidence pointing toward this (colour change of natural indicators in living cells) has been called into question by the author, it still may occur in very thin layers, and has been described for artificial membranes by Bethe and Toropoff. Such "membrane electrolysis" must depend, of course, on a high mobility of H^+ (or OH^-) ion with respect to others present. Whether this is the case in living cells cannot be easily determined, since it is difficult to apply sufficiently high concentrations of H^+ or OH^- ions without damage to protoplasm.

Potassium Effects.—We do know, however, that certain ions, notably potassium, have a pronounced effect which can be interpreted as due to a high mobility. Thus they have both a large "concentration" effect, and a large "chemical" effect (e.g., vs. Na^+ or Li^+). Indeed, the high mobility of K^+ ion has been invoked to account both for the normal P.D. across the protoplasm, and for many of the current flow effects including stimulation itself. There is much to suggest that this is so: high KCl inside cells and low outside them; movement of K^+ ions outward by the stimulating outward currents; paralysing or P.D. depressing action of KCl externally applied. All these are facts, and must find some explanation. That it is not so simple as once thought is, however, indicated by the following results.

Many of the same effects occur in a species of *Halicystis* having no more KCl in the sap than in the sea-water (*Halicystis Osterhoutii* of Bermuda); they also persist nearly unchanged in another species when sea-water is substituted for the KCl of the sap. Many of the directional

effects also continue when artificial sap or natural sap, is applied outside the cells of *Halicystis* or *Valonia*, thereby abolishing the gradients. Finally, although KCl has a remarkable effect in causing stimulation in *Nitella*, and in inhibiting spontaneous recovery therefrom, the flow of inward current, carrying largely K^+ ions inward, can cause recovery of positive P.D. while it flows (see below). Some source of potential, and reason for stimulation, other than the KCl gradient, important though that is, must be sought, in the author's opinion. What that might be is indicated below, after the following section.

Restorative Effects.—In addition to the striking alterations produced by outward current flow, inward current may also do more than merely polarise an existing membrane. Under certain conditions, which suggest that the cell surface lacks its normal electrical properties, inward current flow of sufficient density and duration may actually restore the missing properties. Thus *Valonia*, when freshly gathered and cleaned, or when recovering from the injuries of impalement, may display a purely ohmic, non-reactive resistance; it might be taken for a dead cell, or at least a permanently "stimulated" one, with low P.D. and no polarisation, either to small inward or outward currents. If a sufficiently large inward current is passed, however, the cell suddenly "awakes," a counter-E.M.F. appears, in a sigmoid time course and a definite threshold; a large positive P.D. up to 200 or even 300 mv. may appear as long as the current flows, and it may take several seconds to disappear on break of current, in a slow, linear, non-exponential curve, suggesting rather the falling away of a stable positive P.D. than of a transient polarisation. Something has been restored that persists, even after the large P.D. has disappeared; for now we find that succeeding current flows of the same density produce this effect much more quickly. Not only this but much smaller currents are now effective, which had no effect at all before. This is even true for outward currents; these, however, tend to destroy the new polarisability while they flow, with recessions and steadily falling effects on repetition. Time also, between current flows, tends to cause loss of the polarisability induced by the original large inward flow. The "conditioning" or "restoration" of polarisability may even extend to producing nearly regular polarisation curves, about as exponential as ever obtain in *Valonia*. Apparently both a tendency to positive P.D. and more regular capacity effects results from inward flow. A clue as to the mechanism is supplied by *Halicystis*. When this is treated with sufficient ammonia to reverse its P.D. spontaneously, the passage of large inward currents now tends to restore positivity, not only while they flow, but for a time thereafter, just as in *Valonia*. (Cf. also the restorative effects of inward currents at just sub-threshold ammonia concentrations in *Halicystis*.) Furthermore, *Valonia* cells which have reached the regular polarisability and high effective resistance mentioned early in this paper can be made to display delayed and irregular polarisation by dilute ammonia. Inward current flow then has the restorative effects first mentioned in this section. On the other hand, treatment by certain weak acids will promptly restore regular polarisability and high resistance to cells lacking these, due to ammonia or otherwise.

The strong suggestion emerges from these facts that inward current may act by increasing acidity at some critical surface, possibly by desaponification or actual migration of some fatty acid which had been saponified or otherwise dispersed. This mechanism for current flow

effects is based, however, only on analogy, and it may turn out that current flow resembles acid or alkali effects only by operating upon the same essential structures or membranes; not by the same chemical action. In either case, however, the importance of the membrane is emphasised, as well as its remarkable, usually "all-or-none" lability.

Maintenance of Membranes and Gradients.—A final word may indicate the direction in which present work is going on some of the large plant cells. It seemed increasingly evident that inorganic ion gradients, *e.g.*, between sap and sea-water, had little to do with many of the electrical effects. Yet both P.D. and appreciable currents were steadily maintained during the life of the cells, indicating some source of energy. In organisms this must eventually be metabolic energy, derived from the oxidation or other alterations of food materials—in plants, of course, manufactured by their own photosynthesis. Some connection with metabolism is unescapable, both for the electrical and other activities of cells (*e.g.*, salt accumulation). The steps by which it is linked remain the problem. How much of the recognised dependence of P.D. upon temperature, oxygen, light, stimulants, poisons, etc., is direct, and due for example to altered diffusion gradients of ions, inorganic or organic? How much is due to the maintenance of the remarkable biological membranes themselves, or to their alterations under metabolic influence? It is too early to unravel this problem yet, but there is evidence accumulating that many of the effects are indirect. Thus temperature and light may strongly influence respiration and photosynthesis, yet have little direct effect upon P.D. and polarisability. However, in the presence of altered O_2 , CO_2 , ammonia, p_H , etc., the effects of these physical changes may become extremely great. Energy is probably expended, for example, in the spontaneous recovery from stimulation, during current flow or after in *Nitella*. That is now under measurement, for comparison with similar repair processes in nerve. Which of the many possible organic materials, ions, oxidants, reductants, etc., involved in metabolism supply the actual gradients giving the normal potentials; and how are these altered under current flow, to destroy or restore the membrane properties? These are but a few of the questions connected with natural membranes, which these large plant cells prompt us to ask, and incite us to study. We hope that proper artificial membranes can do as much and suggest the answers.

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THE PROTOPLASMIC SURFACE IN CERTAIN PLANT CELLS.

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Certain large multinucleate plant cells, offering especial advantages for the study of this subject, will be briefly considered. They belong to the marine plants *Valonia* and *Halicystis*, and to *Nitella* which lives in fresh water.

The protoplasm forms a thin layer having an inner non-aqueous surface, an aqueous layer, and an outer non-aqueous surface protected

by a cellulose wall (this is so permeable that it may be neglected in the discussion). The protoplasm surrounds a large vacuole filled with watery sap. The nature of the surface will be considered under the following heads:—

1. It Behaves as a Liquid.—The surface of the protoplasm in contact with the sap of the vacuole behaves like an oily liquid and appears to display true surface tension. This is also true of the outer surface when protoplasm is squeezed out of the cell. Such a liquid might have oriented molecules at its boundary but these would not necessarily determine its entire behaviour.

If the protoplasmic surface consisted of a thin solid membrane¹ it might behave in many respects like a liquid,² but it would have to be highly extensible in certain cases. For example, the very long thin threads of protoplasm traversing the vacuoles of certain cells of flowering plants sometimes break in two and both parts then round up and are retracted by the protoplasm, involving a great decrease of surface area.

A layer forming the protoplasmic surface should not be confused with one lying outside the protoplasm, such as the cellulose wall of plant cells or the chitinous covering of many animal cells. Owing to the presence of such coverings it is difficult to find "naked protoplasm" except possibly at the surface of the vacuole in plant cells.

In this connection let us consider certain epidermal cells of plants. The cellulose wall when first formed is highly permeable to water and to electrolytes. But the outer wall, exposed to the air, becomes impregnated with waxy substances and then acts much more like the non-aqueous protoplasmic surface. Hence when solutions are placed on the outer surface of the epidermis its reaction in respect to permeability and electrical behaviour may resemble that of the protoplasm although showing little alteration when the cells are killed. If the whole cell were covered with such a waxy cell wall which was so thin as to be invisible and which become disrupted when the cell was killed it might be difficult or impossible to distinguish between it and the non-aqueous protoplasmic surface.

2. It has a Low Dielectric Constant.—This is indicated by its imiscibility with water. Its high impedance³ and effective resistance (250,000 ohms per square centimeter in *Nitella*) indicate that it permits little dissociation and is largely impermeable to ions,⁴ as is the case with

¹ Cole, K. S., *J. Cell. and Comp. Physiol.*, 1932, 1, 1; Cole, K. S. and Michaelis, E. M., *ibid.*, 1932-33, 2, 121; Harvey, E. N. and Danielli, J. F., *ibid.*, 1936, 8, 31; Harvey, E. N., *ibid.*, 1936, 8, 251; Shapiro, H. and Harvey, E. N., *ibid.*, 1936, 8, 21; Danielli, H. F. and Davson, H., *ibid.*, 1935, 5, 495.

² But the tension would presumably augment as the surface was extended which would not be the case with a liquid.

³ Blinks, L. R., *Science*, 1928, 68, 235; *J. Gen. Physiol.*, 1929-30, 13, 223, 361, 495, 793; 1930-31, 14, 127, 139; 1932-33, 16, 147; 1933-34, 17, 109; 1934-35, 18, 409; 1935-36, 19, 633, 673, 867; 1936-37, 20, 229; Cold Spring Harbor symposia on quantitative biology, 1936, 4, 34; Blinks, L. R., Rhodes, R. D. and McCallum, G. A., *Proc. Nat. Acad. Sci.*, 1935, 21, 123. Cole, K. S., *J. Gen. Physiol.*, 1928-29, 12, 29, 37; 1934-35, 18, 877; Cold Spring Harbor symposia on quantitative biology, 1933, 1, 107, 131; Cole, K. S., and Cole, R. H., *J. Gen. Physiol.*, 1935-36, 19, 609, 625; Cole, K. S., and Curtis, H. J., Cold Spring Harbor symposia on quantitative biology, 1936, 4, 73. Fricke, H., *Physic. Rev.*, 1925, 26, 682; *J. Gen. Physiol.*, 1925-26, 9, 137; Fricke, H. and Curtis, H. J., *Nature*, 1934, 133, 651; 134, 102; 1936, 135, 136; *J. Gen. Physiol.*, 1934-35, 18, 821.

⁴ Relatively few ions in the layer will suffice to give the values found in measurements of potential difference.

substances of low dielectric constant. (In guaiacol with a dielectric constant of about 14 KCl and NaCl are weak electrolytes with a dissociation constant⁵ of about 10^{-5} .)

This is also shown by P. D. measurements. For example, we find a P.D. of 85 mv. between a region of *Nitella* in contact with 0.01 *M* KCl and one in contact with 0.01 *M* NaCl; we also find about 54 mv. between a spot in contact with 0.01 *M* KCl and one in contact with 0.001 *M* KCl.

This shows that the surface differs greatly from water. We cannot imitate it by a protein film imbibed with water, but we succeed very much better when we employ organic solvents, immiscible with water, which have low dielectric constants. The value found with two concentrations of KCl can be obtained with various organic solvents.⁶ With guaiacol KCl is much more negative to NaCl than in an aqueous system and thus imitates *Nitella*, *Valonia* and *Halicystis*. (Although a well-dried collodion membrane imitates the "concentration effect" between 0.1 and 0.01 *M* KCl it acts quite differently from *Valonia* where $U_K > V_{Cl} > U_{Na}$ and $U_H > V_{Cl} > U_{Na}$; but this order is found in certain non-aqueous solvents.)⁷

In respect to permeability the protoplasmic surface in these cells behaves in many respects like guaiacol⁸ which resembles *Valonia* in that the order of penetration is $K > Na > Ca$, Mg and also in that $Cl > SO_4$ (all entering very slowly as compared with ethyl alcohol). Guaiacol differs from well-dried collodion in admitting at the same time anions, cations, and water, and in this respect it resembles *Valonia*.

3. The Surface Appears to be Acid in Nature in *Valonia*.⁹—The experiments¹⁰ indicate that NH_3 enters by forming a compound with an acid, which we may call HX , in the protoplasmic surface according to the scheme $NH_3 + HX \rightleftharpoons NH_4X$. This also applies to the strong base guanidine.^{11(a)}

On the other hand, H_2S enters by simple diffusion.^{11(b)} Experiments^{11(c)} made by adding HI to the sea water show that the iodide enters chiefly as NaI. These results indicate that the surface is acid in character.

4. It is not Homogeneous.—The experiments indicate that certain substances can be removed from the surface without causing its disintegration. This removal changes its properties but the normal behaviour returns when the substances are replaced. An example is seen in *Nitella* when the irritability disappears after cells have been kept for two or three days in distilled water. The water then contains substances which, when collected and placed on the cell, restore its normal properties.¹² For convenience these substances have been called *R*.

Under normal conditions *R* appears to be supplied to the surface

⁵ Shedlovsky, T., and Uhlig, H. H., *J. Gen. Physiol.*, 1933-34, **17**, 563.

⁶ Unpublished results. Also Bentner, R., *Die Entstehung elektrischer Ströme in lebenden Geweben*, Stuttgart, Ferdinand Enke, 1920.

⁷ Meyer, K. H., Hauptmann, H. and Sievers, J. F., *Helv. chim. acta*, 1936, **19**, 948.

⁸ Osterhout, W. J. V., *Ergebn. Physiol.*, 1933, **35**, 967; *Bot. Rev.*, 1936, **2**, 283. The dielectric constant of guaiacol saturated with water is 14.3 at 25° C.

⁹ *Nitella* and *Halicystis* have not been adequately tested in this respect.

¹⁰ Osterhout, W. J. V., *Proc. Nat. Acad. Sci.*, 1935, **21**, 125.

^{11(a)} Jacques, A. G., *Proc. Nat. Acad. Sci.*, 1935, **21**, 488; (b) *J. Gen. Physiol.*, 1935-36, **19**, 397; (c) unpublished results.

¹² Osterhout, W. J. V., and Hill, S. E., *Proc. Soc. Exp. Biol. and Med.*, 1934-35, **32**, 715.

from the interior of the cell¹³ as fast as it dissolves out in the pond water, but when calcium is absent *R* comes out more rapidly so that the surface is impoverished and irritability¹⁴ is lost. At the same time the potassium effect disappears,¹⁵ i.e., the ability of the cell to discriminate electrically between sodium and potassium (under the proper conditions the cell acts somewhat like a potassium electrode when placed in a mixture of sodium chloride and potassium chloride).

Substances which act like *R* in restoring irritability and the potassium effect are found in blood, urine, and saliva which suggests that muscle and nerve may resemble *Nitella* in these respects.

Among the substances which can restore one or both of these properties are NH_3 , NH_4Cl , tetraethyl ammonium chloride, guanidine, and adrenaline.¹²

Another example is found in *Valonia* where treatment with guaiacol¹⁶ (which does not injure the cell) changes the apparent mobilities in the protoplasmic surface. Before treatment we find the ratio $U_{\text{K}} \div V_{\text{Cl}} = 20$ and $U_{\text{Na}} \div V_{\text{Cl}} = 0.2$, but after treatment we have $U_{\text{K}} \div V_{\text{Cl}} = 0.36$ and $U_{\text{Na}} \div V_{\text{Cl}} = 4.5$.

These changes may depend on alterations in compounds or in charged complexes (in the sense of Kraus)¹⁷ like KZ^+ (where *Z* is an element or a radical). But this does not alter the essential point which is that great changes are possible and this indicates that the surface is not homogeneous.

We know that a variety of substances pass in and out through the surface and that the cell contains a variety of surface-active substances which would tend to accumulate in the surface. We may therefore conclude that it cannot be homogeneous.

5. Its Thickness.—Fricke¹⁸ arrived at a value of 33 Å for the thickness of the non-aqueous surface layer of the erythrocyte, assuming a dielectric constant of 3. If composed of fatty acid it might be unimolecular, but if we suppose it to consist of a substance like guaiacol the calculation comes out differently. Assuming the dielectric constant¹⁹ of the guaiacol²⁰ to be 14.3 throughout the layer and the diameter⁵ of the molecule to be 6 Å the layer would be 26 molecules thick. Until we know more about the actual composition of the surface such estimates are open to question.

As the result of his recent experiments, Fricke believes that the surface layer is more than one molecule in thickness. This is also the conclusion of Schmitt, Bear, and Ponder,²¹ who studied the behaviour of the surface with polarised light.

These remarks apply to a surface with static capacity (which is independent of frequency). Blinks states that in *Valonia* polarisation

¹³ Osterhout, W. J. V., *Ergebn. Physiol.*, 1933, **35**, 967; *Physiol. Rev.*, 1936, **16**, 216.

¹⁴ This term is here used, as in nerve physiology, to mean ability to give action currents when stimulated electrically.

¹⁵ We find about 85 mv. on leading off from a spot in contact with 0.01 *M* KCl to one in contact with 0.01 *M* NaCl.

¹⁶ Osterhout, W. J. V., *J. Gen. Physiol.*, 1936-37, **20**, 13.

¹⁷ Kraus, C. A., *Trans. Electrochem. Soc.*, 1934, **66**, 179.

¹⁸ Fricke, H., *J. Gen. Physiol.*, 1925-26, **9**, 137.

¹⁹ Using this dielectric constant we obtain for the thickness of the layer 157 Å.

²⁰ Shedlovsky, T., and Uhlig, H. H., *J. Gen. Physiol.*, 1933-34, **17**, 549.

²¹ Schmitt, F. O., Bear, R. S., and Ponder, E., *J. Cell. and Comp. Physiol.*, 1936-37, **9**, 89.

capacity (varying with frequency) appears to play the chief rôle. In that case we can set no limits to the thickness of the non-aqueous surface layer.

If the non-aqueous surface layer is not homogeneous and if it can lose a part of its substance without disintegrating it can hardly be regarded as a single layer of molecules. If it is several molecules thick its surface molecules may be oriented, but these will not necessarily determine its entire behaviour.

The non-aqueous surface layer must be thick enough to make the passage of certain substances a million times slower than in water.²²

6. Its Formation.—This presents an interesting problem. Many substances diminish surface tension and might therefore be expected to move into the surface where separate phases might be formed.²³ But in that case we should expect both inner and outer surfaces to be alike so that there would be no E.M.F. with sap on both sides of the protoplasm. This is not true of any of these cells. For example, the protoplasm of *Halicystis* with sap on both sides shows an E.M.F. of about 70 mv., indicating a considerable difference between the inner and outer surfaces.

7. Chemical and Physical Research.—The non-aqueous surface layer interests the biologist because it controls metabolism by determining what can enter and leave the cell and because it is responsible for bioelectrical phenomena. It also presents problems of interest to the physicist and chemist,²⁴ involving all sorts of surface phenomena as well as the behaviour in organic solvents of partition coefficients, ionic mobilities, and diffusion constants.

Until such matters have been investigated by the chemist and physicist the biologist cannot hope for rapid progress. In this connection attention may be called to recent work with guaiacol which is employed in models because to some extent it imitates the behaviour of certain protoplasmic surfaces. The kinetics of diffusion in these models presents interesting features which have been elucidated by Longworth²⁵ who has also studied moving boundaries in guaiacol. The order of penetration of alkali guaiacولات follows that of the mobilities of their cations in water. This is because their partition coefficients also follow this order. Shedlovsky and Uhlig^{5, 20} explain this as the effect of the ionic radius. They have measured dissociation constants and ionic mobilities in guaiacol.

Continuing these studies we have recently found the following:—

When a layer of guaiacol (B) is in contact with an aqueous solution (A) of trichloroacetic acid both acid and water diffuse into the guaiacol. We now place distilled water (C) in contact with the other side of B. Acid then diffuses from the guaiacol phase (B) into the

²² Jacques, A. G., unpublished results. The protoplasm is almost impermeable to CaSO_4 , MgSO_4 , and CsCl (see Osterhout, W. J. V., *Ergebn. Physiol.*, 1933, 35, 981 (Table I.); also Cooper, W. C., Jr., Dorcas, M. J., and Osterhout, W. J. V., *J. Gen. Physiol.*, 1928-29, 12, 427. See also Collander, R., and Bärklund, H., *Acta bot. fenn.*, 1933, 11, 5).

²³ Blinks, L. R., Remarks on W. J. V. Osterhout's paper on electrical behaviour of large plant cells, Cold Spring Harbor symposia on quantitative biology, 1933, 1, 129.

²⁴ It would, for example, be interesting to find what organic substance enables the surface of *Nitella* to act almost like a potassium electrode in a mixture of KCl and NaCl .

²⁵ Longworth, L. G., *J. Gen. Physiol.*, 1933-34, 17, 211; 1934-35, 18, 627; Cold Spring Harbor symposia on quantitative biology, 1934, 2, 218.

distilled water (C). But water moves into C along with the acid. This is because the acid increases the solubility of water in the guaiacol phase and thus causes more water to pass from A to B. But when the acid passes from B to C the solubility of water in B decreases and water moves from B to C. As the freezing-point of A is lower than that of C the water passes from a region of lower to one of higher activity, *i.e.* from a concentrated to a dilute solution. The higher the concentration of acid in A the greater the movement of water into C.

As in some respects guaiacol acts like certain protoplasmic surfaces it seems possible that similar phenomena occur in living cells.

From such experiences we have gained the impression that this is a promising field of research. It is to be hoped that chemists and physicists may cultivate it intensively with corresponding benefits to biology.

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SELECTIVE ACCUMULATION WITH REFERENCE TO ION EXCHANGE BY THE PROTOPLASM.

By S. C. BROOKS.

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The problem of why ions are found in cells in greater concentration than in the external solution bathing them has not been adequately solved. Various mechanisms have been used to explain this phenomenon. The permeability of living cells has been likened to that of dried collodion membranes, especially because of the fact that both seem to be more permeable to potassium ions than to those of sodium. In many cases, as also in the case of the much discussed alga, *Valonia*, the concentration gradient must be accounted for in other ways besides that of the laws of diffusion alone. Nor could the Donnan equilibrium principle alone account for such facts as the accumulation of potassium within some cells to a concentration many times exceeding that in the surrounding medium, while at the same time sodium was present in but a fraction of its "outside" concentration.

The first important contribution to the study of this question was made by Andre and Demoussy,¹ who explained the relative abundance of potassium as compared with sodium in sugar beets, and the change with location and with time, of the ratio between the two, by making the fundamental postulate that equilibrium was not attained during the time studied. The writer has offered in the past a mechanism of selective penetration of ions based upon the mobility of ions and ion exchange in a membrane which may be designated as mosaic in structure under conditions of a non-equilibrium state. This theory with certain modifications and additional experimental evidence will be discussed.

¹ Andre, G., and Demoussy, E., *Bull. Soc. Chim. Biol.*, 1925, **7**, 806-10.

Since the cell is constantly growing while alive, it never attains equilibrium. The continuous metabolism affords a constant source of H and HCO_3^- ion, and only when this process stops is there a return to equilibrium between outside and inside. Besides respiration, there appears to be present in most tissues a slight amount of glycolysis and in abnormal tissues a great amount as described by Warburg. This process also produces a supply of H and an anion other than HCO_3^- . The relation between high levels of metabolic activity and accumulation of ions has been demonstrated experimentally by the work, for example, of Hoagland and Davis,² in which bromine ion is accumulated to a marked degree by *Elodea* in concentrations greatly in excess of those in the external solution. The relation between ion uptake and glycolysis has been shown in tumor tissues which are rich in K^+ . These metabolic processes then are the source of H^+ and HCO_3^- and other anions in the cell.

If the interior of the cell contains a concentration of carbon dioxide greater than that in the exterior a great excess of hydrogen ions and bicarbonate ions arises. Hydrogen ions will, therefore, move outward through the mosaic surface, but since no ions can accompany them, the maintenance of electrical neutrality will necessitate that other cations should enter the cell in amounts electrically equivalent to the hydrogen ion leaving the cell. Therefore, at equilibrium $\frac{[\text{H}^+]_i}{[\text{H}^+]_o} = \frac{[\text{K}^+]_i}{[\text{K}^+]_o}$. We

can thus account for the accumulation of any ion in the sap of a living cell up to a concentration at which the ratio of its activity in the surrounding solution is equal to the same ratio for the hydrogen ion. In this process of ion exchange the amount of each cation taken in will be proportional to the product of two factors; the activity gradient for that ion in the direction of entry into the cell and its mobility through the protoplasm. Although there is less potassium than sodium in seawater its superior mobility would easily account for the fact that more potassium than sodium is exchanged for hydrogen ions. The absence inside the cell of bivalent ions may be readily explained by their low penetrability together with their low activities in sea-water. In the meantime HCO_3^- is being exchanged through the anion permeable areas for Cl^- . The slightly greater mobility of I^- may account for its accumulation by many algae.

The experiments with plants in which the sap cannot be extracted from the rest of the plant, such as *Elodea*, potato and barley, are only roughly comparable to those on *Valonia* and *Nitella*. In the former group the whole plant is subject to analysis, while in the latter accumulation of ions can be followed through the protoplasm and sap respectively.

In the experiments with *Valonia* and *Nitella* in which the sap can be extracted free from the rest of the plant, emphasis has heretofore been placed on the ratio between K ions in the sap as compared with that in the external solution. The same reasoning has applied concerning the respective H ion concentration of these two solutions. In the present paper it is suggested that the original ion exchange theory in which K^+ exchanges for H^+ and Cl^- for HCO_3^- or unknown anion be modified to include some intermediary steps in which K^+ and Cl^- respectively first form a compound with some constituent of the protoplasm before exchanging with an H or HCO_3^- ion in the sap.

² Hoagland, D. R., and Davis, A. R., *Protoplasm*, No. 4, 1929, 6, 610-626.

Experimental.

Experiments of the writer, some of which are unpublished, seem to show that the protoplasm accumulates ions before sending them on into the sap. There are three separate electrolytes which have been found to be concentrated in the protoplasm to a greater extent than in the sap or the external solution; Rb Cl, radio active K and methylene blue.

The writer³ found that, in making the analysis of the sap of *Valonia* which had been immersed in solutions containing Rb for some time and of the Rb containing solutions in which the plants had remained, a certain amount of Rb was calculated to have been taken up by the protoplasm in high concentration. In the absence of exact knowledge of the dimensions of the protoplasmic layer, it is difficult to evaluate the exact degree of accumulation in the protoplasm of these plants.

Recent preliminary experiments of the writer with radio-active K indicate that this substance accumulated to a marked degree in the protoplasm. The experiments were briefly stated as follows: *Nitella* cells were placed in 0.01M solutions of radio-active KCl for 6 hours. At the end of that time a few cells were taken out, rinsed off and dried, the sap extracted and roughly equivalent samples of the sap, wall and protoplasm, and external solution were placed over the Geiger counter, which registers the impacts of β particles. There were very few impacts from the external solution or the sap, but the protoplasm and wall produced a bombardment. Since the half-life of radio-active ^{42}K is 12 hours, the absence of effect in the case of external solution could not be due to decrease in activity during that period. There seemed to be no apparent injury by this treatment of control cells which remained normal for days afterwards. These experiments are at this time merely roughly quantitative and the work is being continued, but they serve to illustrate the theory that there is an accumulation of K ions in the protoplasm before they appear in the sap.

The third case in point of view of this discussion is that of methylene blue, which is completely dissociated at all p_{H} values. In the experiments of M. M. Brooks⁴ with the penetration of this dye into *Valonia*, it was found that dye disappeared from the external solution, and the wall and protoplasm became deeply dyed when the colour of dye in the sap was still very pale, indicating a "heaping up" of the dye before a gradient was established which permitted its entrance into the sap.

Rôle of Protoplasm.

In attempting to account for the accumulation of either Rb or K or radio-active K or the dye cation, the following explanation has been offered: Since protoplasm is not a homogeneous substance it, therefore, has no one p_{H} value. We can conceive of it as consisting of different regions, each having its own p_{H} value, or as consisting of different groups of protein molecules. The concept I wish to present is that of molecular areas rather than of layers or phases of larger dimensions; that different proteins are differently ionised and there would presumably be different gradients depending upon the constitution of the protein molecule. Those molecules which are concerned with photosynthesis would dissociate basic groups and those dealing with the functions of metabolism would dissociate acid groups. In other words, there would be areas of molecular dimensions with all degrees of plus charges and others with all degrees of negative charges, so that cations could exchange with cations in the first case, and anions with anions in the second. Since proteins are amphoteric a cation and an anion could conceivably be displaced

³ Brooks, S. C., *Jour. Cell. & Comp. Physiol.*, No. 2, 1935, 6, 169-180.

⁴ Brooks, M. M., *Amer. Jour. Phys.*, No. 2, 1926, 76, 360-379.

from the same protein molecule. Since protein molecules have high valency it is conceivable that a comparatively large number of acidic or basic groups could be displaced from one molecule by K^+ and Cl^- entering, thus producing accumulation. This is the theory underlying the mosaic idea, rather than the existence of definite delimited areas of cation or anion permeability. In this way the electrical neutrality of the protoplasm would be kept balanced, and there would be no necessity for supposing that there are definite periods in which one or the other would predominate.⁵ These differences would exist continuously so long as metabolism were going on.

Potential differences have been measured by Brooks and Gelfan⁸ between the external solution and the inside layer of the protoplasm by means of micro-saltbridges. Since there exists a P.D. between the outside layer and the inside, this is consistent with the concept that the molecules forming the inside layer have a different dissociation constant from those towards the external solution.

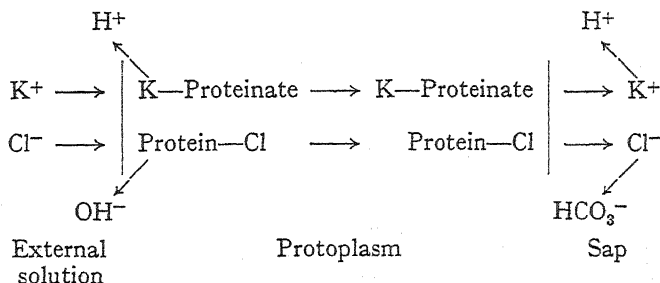


FIG. I.

Fig. 1 gives an illustration of what may take place. K^+ unites with a H-proteinate and Cl^- with a protein-OH. The proteins are sufficiently supplied with free basic and acidic groups. A number of these may be displaced simultaneously. The K-proteinate and protein-Cl thus formed then migrate, uniting with the basic and acidic groups of adjacent molecules, and so move on through the protoplasm until they come to the molecules adjacent to the sap. Exchange with H^+ and HCO_3^- then takes place.

If H and OH were displaced they could unite to form water or some organic weak acid which may diffuse either outwards or into the sap. Small concentrations of an organic acid have been demonstrated in the sap.

It is interesting to contrast the behaviour in acid solutions of the protoplasm of a plant like *Valonia* which has a normal habitat which is alkaline (8.0 to 8.2) with that of *Nitella* which lives normally in pond water or an acid environment. In the former case the penetration of K is stopped when the external solution is made acid and K comes out.⁷ In the latter case if the external solution has a p_H of 6.0, penetration of K continues. It should be noted that the p_H of the sap of *Valonia* is 6.0 and that of *Nitella* in this case 5.7. In either case the gradient of H^+ is outward. In those cases where the p_H was lowered to 5.0 and yet the

⁵ Briggs, G. E., *Proc. Roy. Soc., B*, 1930, **107**, 248-269.

⁶ Brooks, S. C., and Gelfan, S., *Protoplasm*, No. 1, 1928, **5**, 86-96.

⁷ Jacques, A. G., and Osterhout, W. J. V., *Proc. Soc. Exptl. Biol. & Med.*, No. 9, 1934, **31**, II21-II22.

penetration of K took place no data have been obtained concerning the p_H of the sap. One might conclude that the dissociation of the proteins of the two plants is entirely different; for example, that of *Valonia* may have a higher concentration of basic groups and that of *Nitella* more acidic groups.

It has frequently been noted that injury is accompanied by exosmosis of K and Cl. This may be correlated with the breakdown of the mechanism of accumulation in which too many of the replaceable ions have been exchanged and the gradient is reversed.

In the experiments of M. M. Brooks^{*} on the penetration of mineral acids into *Valonia* from a high H ion concentration in the external solution, it was found that the concentration of H_2CO_3 in the sap was at first increased. This lasted for some time before the p_H of the sap was lowered by the mineral acid. This has been interpreted to mean that the carbonates and bicarbonates of the protoplasm were being displaced by the penetrating acid and used up first,—i.e., the cations were being displaced by H ion, H_2CO_3 being free to diffuse into the sap. This continues until no more carbonates and bicarbonates are left for exchange, after which the mineral acid is observed in the sap. This seems to be additional evidence that penetrating substances form temporary associations with the protoplasm before passing into the sap.

The Rôle of the Sap.

The rôle of the sap in accumulation is, therefore, quite secondary. In discussing the rôle of the sap with reference to the rest of the cell, it may be considered as the last link in the chain of ion exchange. The K and Cl ions exchange with H^+ and HCO_3^- in the sap, which is always present while the plant is alive.

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^{*} Brooks, M. M., *Reprint Pub. Health Repts.*, No. 26, 1923, 38, 1449-1470.

SALT ACCUMULATION BY PLANTS—THE RÔLE OF GROWTH AND METABOLISM.

By F. C. STEWARD.

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Accumulation and Osmotic Work.—Salt accumulation—which denotes the absorption of salts from dilute * solutions by cells which attain high † concentrations in their internal fluids (vacuoles)—entails simultaneous movements of anions and cations not in accord with concentration gradients. The problem is not one of equilibria. The

* Provided the supply is maintained many plants can absorb their salts from solutions of extreme dilution (e.g. order of 5.0 p.p.m. for PO_4 and K, see *Plant Physiol.*, 1929, 4, 213, and *Soil Science*, 1929, 27.

† The (K) of the sap of flowering plants is commonly of the order of 50 to 100 mgm. equivs. per litre.

transfer of salt from external solution to cell sap tends to increase their total energy and work must be done and energy expended. The living cells thus evade the limitations of true thermodynamic equilibrium—a condition they rapidly approach when killed, or deprived of oxygen—by means of their own metabolism. Since the explanation of the impressive concentration gradients which may exist across the protoplasmic surface must entail the rôle of metabolism, the nature of the relation between vital processes and salt accumulation is here described.

Plant physiologists have been loath to admit that cells are capable of osmotic work. The water relations of plant cells are commonly interpreted without recourse to this view. On the contrary water movements in the animal body which do not accord with osmotic gradients (e.g., the familiar case of the kidney) imply that cells and organs do work. The teleost fishes in fresh water conserve their salt content and eliminate water and in sea water eliminate excess salts and conserve water. Both these processes demand osmotic work, the site of the former being the kidney and the latter the gills.¹ Bennet-Clark² now suggests for plants that “potentially growing cells”—which it will be seen later are also capable of salt accumulation—may possess an active mechanism for the secretion of water into the vacuole.

Models and Permeability.—A popular trend in physiology is to eliminate the complexities of the living system and to interpret its behaviour by analogy with so-called “model” experiments *in vitro*. The very complexities thus eliminated—respiration, protein and carbohydrate metabolism, growth—on the basis of investigations to be summarised become the salient features of cells active in salt accumulation.

The evidence indicates that salt accumulation cannot be considered merely as a passive property of a membrane endowed with special permeability properties. The membranes *in vivo*, through which entering ions must pass, also represent boundary surfaces at which reactions and energy exchanges may occur, and their permeability properties alone do not suffice for salt accumulation. The applicability of Fick's Law to those cases which involve permeability alone emphasises that accumulation involves supplementary mechanisms—a fact recognised by Collander.³ The remarks which follow do not entail rigorous definition of the nature and structure of the functional membrane.

Primary and Induced Effects in Salt Uptake.—All cases of uptake of salt or ions are not of the same kind. Commonly anions and cations are absorbed simultaneously and, in the case of alkali halides (KCl, or KBr) often in approximately chemically equivalent amounts. This can occur without loss of other ions (except CO₂) from the cells, thus producing a gain of total salt content and an increase in the electrical conductivity of the sap⁴ (see Fig. 2). This type of absorption which represents the major problem of salt uptake by cells⁵ has been designated “Primary Absorption.” Cells in which growth has subsided may still absorb ions by exchange for those previously accumulated. The

¹ Keys, A. B., *Proc. Roy. Soc., B.*, **112**, 183.

² Bennet-Clark, T. A., Greenwood, A. D., and Barker, J. W., *New Phytol.*, **1936**, **35**, 277.

³ Collander, R., 1937. *This vol.*, p. 985.

⁴ (a) Hoagland, D. R. and Broyer, T. C., *Plant Physiol.*, **1936**, **11**, 471.

(b) Hoagland, D. R., Hibbard, P. L., and Davis, A. R., *J. Gen. Physiol.*, **1926**, **10**, 121. (c) Steward, F. C., *Protoplasma*, **1932**, **15**, 29. (d) Steward, F. C. and Berry, W. E., *J. Expt. Biol.*, **1934**, **11**, 103.

⁵ Steward, F. C., *Ann. Rev. Biochem.*, **1935**, **4**, 519.

exchange of Br for Cl in *Nitella*^{4b, 6} is a case in point. This type of uptake, induced by a change in the composition of the external solution, can be designated as "Induced Absorption" and is often shown by cells less active in metabolism. The interest of the case cited lies in the fact that the process of exchange—like the original "primary" uptake of KCl—necessitated the active participation of metabolic processes. Both processes, in fact, occurred in the same culture though not necessarily in the same cells. To many other absorption phenomena

in which interchange between cells and an external solution occurs the same degree of interest does not apply. The penetration of ammonia into cells may be at the expense of potassium.⁷ Results for potato discs 70 hours at 23° C., in aerated, phosphate buffered, solutions at pH 6.75 containing different concentrations of $(NH_4)_2SO_4$ show this and also that the effect of ammonia is to retard the accumulation of all the other anions and cations investigated (Fig. 1). The rapid uptake by cells of heavy metals, described by Devaux and later by Genevois⁸ and Genaud,⁹ conforms to the mass law and the vital properties are not essentially involved. The familiar uptake and apparent accumulation of many basic dyes by cells proceeds under conditions of oxygen want which would suppress accumulation of neutral salts and is complete in time periods too short for the active participation of metabolism. A case recently investigated by Steward and Harrison illustrates

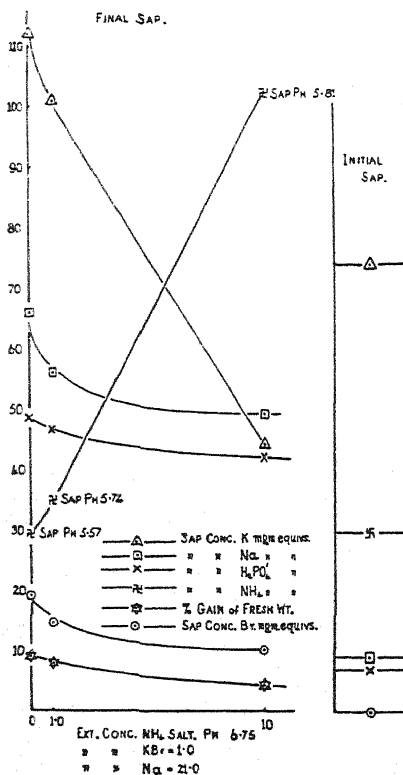


FIG. 1.

the necessity for the distinction between absorption of different types as outlined above.

The slow accumulation of Br from KBr solutions by thin discs of potato tissue is determined by oxygen supply¹⁰ and occurs in cells at the disc surface which exhibit enhanced metabolism and vital activity. In the case of Rb Br the slow accumulation of Rb and Br in chemically equivalent amounts which proceeds unabated for 100 hours and is in every way analogous to the uptake of Br and K from KBr, is preceded

⁶ (a) Hoagland, D. R., and Davis, A. R., *Protoplasma*, 1929, 6, 610. (b) Hoagland, D. R., Hibbard, P. L., and Davis, A. R., *Plant Physiol.*, 1928, 3, 473.

⁷ Compare experiments cited in Osterhout, W. J. V., *Biol. Rev.*, 1931, 6, 369. (b) *Ergebnisse Physiol.*, 1933, 35, 967.

⁸ Genevois, L., *Protoplasma*, 1928, 10, 478.

⁹ Genaud, P., *Ann. Physiolphysicochim. biol.*, 1930, 6, 240.

¹⁰ Steward, F. C., *Protoplasma*, 1933, 18, 208.

by a relatively rapid (complete in not more than five hours in discs 0.75 mm. thick), but strictly limited, absorption of Rb alone which is not confined to active cells at the surface but occurs equally throughout the mass of even thick discs. This uptake of Rb unaccompanied by anion is neither dependent upon oxygen supply nor related to metabolic processes. The distinction between the two types of ion uptake is clear. The first is merely a property of the colloidal substances of the tissue and although, on the basis of concentrations in the total water, "accumulation" (accumulation ratio of 3) may be attained from dilute (0.002 *M*) solutions, this may also occur in tissue killed by alcohol or by other means. This represents a process to which the conceptions of equilibrium apply. The ability of tissue substances to bind or interchange positively charged ions may be the cause of that visible "accumulation" of dye which often occurs in cells from very dilute solutions of basic dyes¹¹ and the homology of which with the accumulation of neutral salts is easily overestimated. Similar phenomena may be responsible for the view expressed by Lundegårdh¹² that the uptake of cations, unlike that of anions, is due to the colloidal properties of cells and is not related to metabolism. Presumably Asprey¹³ was dealing mainly with this property in the uptake of calcium and ammonium from unaerated solutions—an uptake which was complete in a few hours and retarded by other cations. Properties of this kind represent a small and strictly limited part of the cation uptake by actively metabolising cells. On the contrary, the simultaneous and equal uptake of Rb and Br which follows in the potato discs, like that of KBr^{4a, 10} proceeds uniformly for many hours (at least 100 for Rb Br and 140 in case of KBr) represents a process which tends to increase the total energy of the cells and is essentially a property of the living system which does work. It is a significant fact that under the conditions conducive to salt accumulation protoplasmic streaming, visible evidence of the ability of the protoplast to do mechanical work, has been demonstrated¹⁴ in many of the cells concerned.* Only absorption processes of this type will be discussed further in this account.

"Primary" Salt Accumulation and Growth.—Active salt accumulation is clearly dependent upon a capacity for growth. Something more than mere increase of size is here implied. In cellular plants cell division provides a convenient visible indication of their ability to synthesise protoplasm. Plant storage organs provide a diversity of behaviour and include structures (pome fruits, certain bulb scales and cotyledons) the mature cells of which have irreversibly lost the ability to grow and divide. Such tissues^{14a}—even under favourable conditions of temperature and aeration, etc., fail to accumulate the bromide ion. Many common fleshy storage organs (potato, turnip, kohlrabi, etc.) contain cells still able to divide and these are conspicuous

¹¹ See numerous papers of Irwin, M., and Brooks, M. M., and references cited by Osterhout.⁷

¹² Lundegårdh, H. and Burström, H., *Planta*, 1933, 18, 683.

¹³ Asprey, G. F., *Proc. Roy. Soc., B*, 1933, 112, 451.

¹⁴ (a) Berry, W. E. and Steward, F. C., *Ann. Bot.*, 1934, 48, 395. (b) Rosenfels, R. S., *Protoplasma*, 1935, 23, 503. (c) Steward, F. C., Wright, R., and Berry, W. E., *ibid.*, 1932, 16, 576.

* In *Valonia* streaming has only been observed in the minute hapteron cells (the rôle of which in salt uptake has not been considered) and not in the large vesicle. Streaming is a familiar property of *Nitella* cells under conditions conducive to salt accumulation.

by their ability to accumulate bromide from dilute solution.^{14a} It is in a surface zone of cells in the cut discs, in which the synthesis of protoplasm is most evident and in which division readily occurs in moist air, that the salt absorption occurs.^{14c, 15} The visible indications of protoplasmic synthesis can be readily confirmed by direct measurements of protein synthesis in the case of potato discs. Along the axis of a single growing root there exists a gradation both in the ability to accumulate salt and also in growth. Both processes occur most actively near the root apex and decline as cells progressively mature.¹⁶ The distribution of bromide accumulated in leaves shows for the herbaceous shoot a similar tendency, for the greatest concentration of bromide is to be found in the younger most actively growing leaves.^{5, 14b} In *V. ventricosa* the highest halide concentrations occur in the smallest vesicles.^{17b} Large cells or vesicles (*Valonia* and *Nitella*) in which the processes of growth and metabolism are slow, are relatively less active in salt accumulation and in these systems interchange with ions previously absorbed has played a much greater and simultaneous accumulation of anion and cation a much smaller, part in the phenomena observed.

The necessity for active growth may be apparently obscured if roots (barley) are grown with minimal salt supply. These roots accumulate^{4a, 16} during growth high sugar concentrations and subsequently possess for a brief period a great capacity for the accumulation of salt (KBr) which involves the rapid disappearance of sugar. Though much compressed in time this rapid intake is of the same kind as that which normally would have occurred during the growth of the roots and is determined by similar variables as the uptake of salt by storage tissue.^{4a}

The different types of time-absorption curve encountered in storage tissues and excised barley and potato roots are explicable in terms of the previous nutrition and capacity for further growth of the system concerned.¹⁶

The relation between growth and salt accumulation cannot be attributed, as yet, to any given metabolic reaction. In view of the evidence to be summarised later the decline in protein synthesis which is to be expected as growth subsides is suggestive. Granted the system capable of salt accumulation the extent to which this ability is utilised is limited by the following variables which shed further light upon the nature of the process.

The Effect of Light.—The absence of bromide accumulation in *Nitella* in the dark and the relationship between light intensity and duration and bromide accumulation was shown by Hoagland.^{4b, 6, 17a} The effect of light was shown for the entry of bromide in exchange for chloride and also when it was accompanied by cation. These experiments first focussed attention upon the energy relations involved in salt accumulation.

At the outset Hoagland emphasised that the effect of light was not upon permeability. Cells in the dark could attain equality of concentration with their environment.⁴ It was further emphasised that the energy of the light source was not utilised directly but that it operated through those oxidative reactions in which the products of

¹⁵ Steward, F. C., *Protoplasma*, 1932, 17, 436.

¹⁶ Prevot, P. and Steward, F. C., *Plant Physiol.*, 1936, 11, 509.

¹⁷ (a) Hoagland, D. R. and Davis, A. R., *J. Gen. Physiol.*, 1923, 6, 47.

(b) Steward, F. C., and Martin, J. C., *Carn. Inst. Wash. Pub.*, 1937, 475.

photosynthesis are substrates. These experiments, therefore, foreshadowed the later attention to respiration.

It is now clear ^{4, 14b} that in water plants light affects salt uptake, not only by its effect upon the carbohydrate content (see page 1010) of the cells, but it also maintains the aeration conditions (relatively high oxygen and low carbon dioxide concentrations) which are conducive to active absorption.

The Effect of Oxygen.—This is well illustrated by thin discs of storage tissue. In salt solutions aerated by mixtures poorer in oxygen than air the uptake of *both* anion and cation is limited by oxygen concentration. For the uptake of KBr this has been shown for discs of potato,¹⁰ artichoke and carrot,¹⁸ and excised roots of potato.¹⁸ In all the above cases there is a general similarity between the effect of oxygen upon salt accumulation and respiration. However, at zero oxygen concentration salt accumulation tends to disappear although the cells still produce CO₂ anaerobically and in quantity. Aerobic rather than anaerobic metabolic processes are essentially involved in accumulation.¹⁸ Oxygen is not only necessary for salt uptake but also to maintain existing concentrations in the sap.¹⁰ There is ^{4a} outstanding evidence of a similar effect of oxygen supply on the accumulation of the ions K', Br', and NO₃' by barley roots. Excised roots in solutions in equilibrium with air absorbed 80 mgm. equivs. of K per litre of sap in 10 hours, accumulated Br', NO₃' and increased their sap conductivity by 500 per cent. but if in equilibrium with 0.2 per cent. oxygen their increment of [K] and conductivity was slight and neither NO₃' nor Br' were accumulated. The accumulation of bromide by *Elodea* ^{14b} in the dark is conditioned by oxygen tension. The form of the oxygen concentration-salt accumulation curves is the same for storage tissues,^{10, 18} potato roots,¹⁸ and barley roots.^{4a} The only difference is the value of the critical oxygen concentration below which both respiration and salt uptake are limited by oxygen supply.

Other Variables which show the Relation between Salt Uptake and Respiration.—The effect of oxygen concentration upon accumulation and the necessity of aeration for maximum salt uptake ^{4a, c, 14b, 19, 20} suggests that salt accumulation demands a high rate of aerobic respiration.

For discs of storage tissue the same conclusion emerges from the effect of their specific surface. Both the enhanced respiration and salt accumulation are greatest in thin discs of large specific surface,^{14c} and this leads to the view that both processes predominate in a surface zone of active cells.¹⁵

In the effect of temperature on respiration and salt uptake by discs of potato and artichoke the similarity is close (Table I., unpublished data of Steward and Berry).

Rosenfels has published similar results for *Elodea*.^{14b} Both processes have a high temperature coefficient—although its value is dependent upon the range chosen—as was also found for the bromide absorption of *Nitella*.^{4b} In all the work concerned with actively accumulating aerated tissues the effect of temperature is of the same kind for anions and cations. This is shown by Table I. and also by the data ^{4a} for uptake of K, NO₃ and Br by barley roots. The postulate that the

¹⁸ Steward, F. C., Berry, W. E. and Broyer, T. C., *Ann. Bot.*, 1936, **50**, 345.

¹⁹ Petrie, A. H. K., *Austr. J. Expt. Biol. and Med. Sci.*, 1933, **11**, 25.

²⁰ Steward, F. C., *Protoplasma*, 1932, **15**, 497.

external ionic product remains constant over a temperature range²¹ which apparently prompted a rediscussion²² of salt uptake based on the Donnan Equilibrium does not apply.

In dilute solutions the salt uptake of potato discs proceeds at a

TABLE I.

Discs in 2 litres of 0.00075 *M* KBr for 80 hours at 23° C.
Concentrations in mgm. equivs. per litre.

Tissue.	T.	CO ₂ Mgms. gms. × hrs.	Sap [Br].	Ext. Soln. Final [K].
	°C.			
Potato	2.80	0.024	0.50	0.823 *
	7.8	0.042	3.83	0.825 *
	13.8	0.084	14.3	0.674
	23.1	0.195	22.6	0.520
Artichoke	3.0	0.035	2.28	0.718
	7.7	0.051	6.34	0.635
	13.7	0.074	16.9	0.516
	23.1	0.112	27.4	0.503

* Note net loss of K which occurs at low temp. Compare loss of Cl in excess of bromide uptake observed by Rosenfels for *Elodea* at low temperature and the loss of chloride from *Nitella*^{17b} at 5° C.

only be mentioned briefly. *Valonia* sap and sea water differ by approximately 2.8 p_H units. In the scheme of Osterhout this has become the cardinal feature. A striking, hitherto unpublished experiment of

Hoagland (Fig. 2) showed that, in the case of barley roots, accumulation of K and Br occurred even from solutions more acid than p_H 4.0 by plant cells in which the maximum range of sap reactions was from p_H 5.8 to 6.5 and that the uptake of K was but little affected by a variation in external p_H from 8.0 to 3.7. Potassium entered against a steep gradient of $K \times OH$. Even in the case of *V. ventricosa*^{17b} the composition of the sap of vesicles in sea water, as well as the gain of [K] and [Cl] which occurs in the dark in sea water enriched with KCl, tolerates a wide range of [OH] though it responds to very much smaller concentration changes (2.5 to 5 times) in

constant rate for relatively long periods of time (over 100 hours) during which respiration is also approximately constant. Under similar conditions both the accumulation of KBr and respiration of artichoke discs declines with time.^{4d} A very similar behaviour in time of respiration and salt uptake has been observed for *Elodea*.^{14b}

The p_H Relations of Sap and Solution.—This controversial aspect can

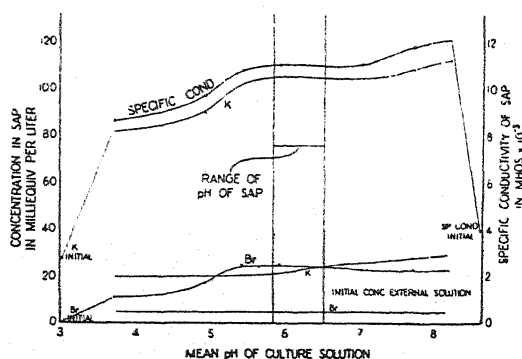


FIG. 2.—Effect of external p_H on accumulation by barley roots. (From hitherto unpublished data of Hoagland.)

²¹ Petrie, A. H. K., *Austr. J. Expt. Biol. and Med. Sci.*, 1927, 4, 169.

²² (a) Briggs, G. E. and Petrie, A. H. K., *Biochem. J.*, 1928, 22, 1071.

(b) Lundegård H. and Burström, H., *Bioch. Z.*, 1935, 277, 223.

external [K]. The sap composition is more closely related to the [K] and [Cl] of sea water than to its [OH].

Hence the suggested mechanism⁷ in which the magnitude and direction of the $K \times OH$ gradient between sap and solution determines the entry and accumulation of K cannot be regarded as of general application. The storage tissues, already rich (of order of 50 to 70 mgm. equivs. K per litre of sap) in potassium accumulate it freely from dilute (less than 0.001 M) solutions not more alkaline than their sap (p_H 5 to 6). In the experiment of Fig. 1 which resembles an oft-quoted experiment on *Valonia* the entry of Na and NH_4 is not inconsistent with the direction of the gradients of "free base," but the latter do not account for the behaviour of K.

The Nature of the Relation between Salt Uptake and Respiration.—This problem has attracted more speculation than experimental investigation. However, in the work on storage tissues* (already cited, together with still unpublished data) roots† and *Elodea*‡ are many simultaneous measurements of respiration and salt uptake under controlled conditions. These investigations are in essential agreement and lead to the following conclusions.

There is no simple quantitative relation between salt accumulation

and respiration but rather a general parallelism between the two processes. Active cells produce carbon dioxide equal to many times the chemical equivalent of the salt absorbed.¹⁰

The effects of salt concentration upon absorption are relatively far greater than upon respiration whereas changes in the total respiration due to oxygen concentration, or temperature produce large effects upon the salt absorbed. The evidence is that the salt uptake is to be related, not to a special component of respiration (*Anionenatmung* of Lundegårdh)¹² which is not exclusively aerobic²² and is due solely to anion uptake, but to the total aerobic respiration rate the magnitude of which is fixed by such factors as the composition of the cells, oxygen concentration and temperature, and is not appreciably affected by the very dilute salt solutions from which accumulation readily proceeds. Clearly it is the oxidative metabolic reactions, of which CO_2 production may be a convenient measure, which are causally related to salt uptake and *not the mere properties of CO_2 as an end product*. This fact alone seriously detracts from the value of the "models" devised by Osterhout and others.^{7b, 23}

TABLE II.

Ext. p_H *.	Sea Water Series, Rel. Sap Conc.†		Sea Water + 0.05M KCl. Rel. Sap Conc.	
	K.	Cl.	K.	Cl.
8.6 to 8.8	103	100	110	106
8.0 to 8.2	100	100	111	108
7.0 to 7.2	101	100	117	114
6.0 to 6.3	101	101	111	108
5.4 to 5.6 ‡	96.5	98.5	107	104

* Regulated by control of CO_2 tension.

† Mean sap conc. in sea water in equil. with air = 100.

‡ Irreversible effects eventually occur at this reaction.

* Carried out in the Depts. of Botany, Leeds University and Birkbeck College.
† Work directed by Prof. D. R. Hoagland, Division of Plant Nutrition, University of California.

²³ Osterhout, W. J. V., and Stanley, W. M., *J. Gen. Physiol.*, 1932, **15**, 667.
(b) Osterhout, W. J. V., and Kamerling, S. E., *ibid.*, 1935, **19**, 167.

Cells in which the salt accumulation is limited by oxygen lack^{10, 14b, 18} or which do not possess the essential properties, as yet only recognisable by their ability to grow and divide, still produce CO_2 in quantity but fail to accumulate salt. The rôle of light in green plants, which renders external aeration superfluous and permits the gain of total salt and uptake of bromide by both *Nitella*^{4b} and *Elodea*^{14b} in excess of the loss of known anions whilst CO_2 is entering the cells, also demands that the emphasis must not be placed exclusively upon the mere exit of CO_2 . The exchange of H^+ for cations, HCO_3^- for anions²⁴ cannot play an indispensable part in the mechanism. Any view which restricts the rôle of respiration solely to anions¹² fails to account for the well-established fact that the uptake of cations is equally linked with respiration and metabolism (see page 1009 for apparent exceptions). The view that the respiration operates upon salt uptake because it regulates the internal reaction of cells overlooks the stability of the p_{H} of the sap of intact plant cells which is commonly stabilised by buffer substances and often by metabolic processes.²⁵ Although H^+ and HCO_3^- derived from respiration may preserve ionic balance when there is great disparity in the uptake of anions and cations this factor cannot be involved when both ions are simultaneously accumulated in equal amounts.

The utility of the relation of salt uptake and respiration is rather that the latter provides an index of the metabolic activity of the tissue and of processes which are linked with accumulation. The rôle of respiration must involve the energy value of the oxidative reactions concerned. Estimates are difficult but, lacking the refinements of calculation suggested by Zschiele,²⁶ the order of the energy used in the accumulation process cannot be more than a small fraction (0.20 per cent.) of the total output of potato discs.¹⁰ The parallelism between aerobic respiration and salt uptake (see effect of oxygen, temperature, etc.) suggests that a relatively constant fraction of the total energy is directed toward salt accumulation.

Biochemical Effects Associated with Salt Uptake.—It is in this aspect that the final clue to the mechanism probably lies.

During active salt accumulation both barley roots (especially from "low salt" plants) and potato discs metabolise relatively large quantities of carbohydrate; in special cases this may be very rapid.^{4a} In some cases in which the activity of roots in salt accumulation is limited by their low sugar content this may be restored by an external supply.^{4a, 16} The activity^{14b} in both salt uptake and respiration of *Elodea* is conditioned by sugar concentration. The stages of oxidative breakdown of sugar which are especially associated with salt accumulation are as yet unknown. Uncertainty which still surrounds the nature of the substrate and the course of respiration in plants is here a limitation. Two suggestive aspects of recent experiments may be mentioned.

The first is drawn from the work of Hoagland²⁷ and suggests that the metabolism of organic acids is involved. When anions not accompanied by cations (e.g., in Ca Br_2 solutions) are absorbed the tissue metabolises organic acids and the loss of organic anion balances the

²⁴ (a) Briggs, G. E., *Proc. Roy. Soc., B*, 1930, 107, 248. (b) Brooks, S. C., *Protoplasma*, 1929, 8, 389.

²⁵ Fife, J. M., and Frampton, V. L., *J. Biol. Chem.*, 1935, 109, 643.

²⁶ Zschiele, P., *Protoplasma*, 1930, 11, 481.

²⁷ Hoagland, D. R., *Soil Science*, 1923, 16, 225.

discrepancy between anion and cation uptake. This does not occur to the same extent when K and Br are simultaneously accumulated. The evidence indicates that equal or unequal uptake of anion and cation is not merely a property of the ions concerned or the reaction of the solutions* but is determined also by the metabolism of the tissue which is in turn regulated by its internal composition (e.g., relative to sugar) and previous nutritional history.

According to the work on potato discs both carbohydrate and nitrogen metabolism are involved. All the variables which affect salt uptake (O_2 supply, temperature, specific surface of discs) have similar effects upon protein synthesis from reserves of alcohol soluble nitrogen compounds. Recent work of C. Preston, in collaboration with the writer, has revealed, under conditions conducive to accumulation,

TABLE III.

Salt.	Conc. per litre Equivs. $\times 10^{-3}$.	Mgms. CO_2 Per Gm. Tissue Per Hour.	Total Sugar Mgms. Per Gm. Tissue.	Alc. Sol. N. Mgms. Per Gm. Tissue.	Alc. In Sol. N. Mgms. Per Gm. Tissue.	% Sol. N. Total N.
—	Initial tissue.		2.99.	1.38.	0.68.	67.
KCl . .	0.75	0.167	8.20	1.15	0.92	55.6
KCl . .	15	0.166	8.32	0.94	1.14	45.2
KCl . .	50	0.188	4.35	0.87	1.16	42.8
KCl . .	75	0.188	4.44	0.85	1.21	41.2
—	Initial tissue.		3.20.	1.37.	0.68.	67.
$CaCl_2$. .	0.75	0.159	8.60	1.19	0.86	58
$CaCl_2$. .	15.0	0.150	9.33	1.24	0.83	60
$CaCl_2$. .	50.0	0.123	10.5	1.34	0.72	65
$CaCl_2$. .	75.0	0.114	10.2	1.37	0.69	66.5

parallel effects of neutral salts upon respiration and protein synthesis which are clearly due to the entry of salt and not to its mere presence in the external solution. In dilute (0.001 *M*) solutions the direct effect of salts (e.g., KCl, KBr) other than nitrates or phosphates on respiration are negligible. With increasing concentration (to 0.075 equivs. per litre) potassium salts cause an increase and equivalent strengths of calcium salts a decrease in respiration and protein synthesis. The contrast between potassium and calcium salts in their effect upon respiration is greatest in the case of nitrates and declines according to the series $NO_3 > Cl > Br$; † and for sulphates these salt effects become insignificant. This series is also that of absorption from salts with a common cation. As modified by salt the respiration does not vary as the sugar concentration but seems more closely connected with the loss of amino-acids and formation of protein. (See Table III.).

* The idea that acid reactions promote the absorption of anions and vice versa is a familiar one.

† $\frac{\text{resp. of tissue in 0.075 equiv. K Salt}}{\text{resp. of tissue in 0.075 equiv. Ca Salt}} = \text{for } NO_3 \text{ 2.40, Cl 1.63, Br 1.32.}$

A similar contrast between potassium and calcium salts is revealed by colour changes which are due to the oxidation in the tissue of aromatic compounds—oxidations which are increased by increasing concentrations of potassium salts and depressed by calcium salts. These salt effects have yet to be imitated in tissue preparations which lack the organisation of the living cell but the oxidations involved are well known and are catalysed by the aerobic oxidases²⁸ of the potato. The consistent parallelism between the intensity of respiration and the oxidations in question (revealed by the response to temperature, oxygen pressure, and the specific surface of the discs) resembles that between respiration and salt accumulation. Thus the oxidases in question appear to be closely associated with the mechanism of cellular oxidation and the neutral salts affect metabolism by their direct effects upon the oxidation mechanism. A possible explanation of the effect of salts upon both respiration and nitrogen metabolism follows, since the oxidation of phenolic compounds by potato oxidases involves the production of ortho-quinones²⁹—substances which deaminate amino-acids³⁰ and thus provide nitrogen (NH_3) for protein synthesis and a deaminated residue for respiration.

Clearly the ion series which represent the ease of uptake of salts with a common anion (K , Na , Ca , Mg , Sr , Li)³¹ or common cation (NO_3 , Cl , HCO_3 , PO_4 , SO_4)²⁷ and which are commonly ascribed to the effects of ionic mobility need to be re-examined on the basis of the metabolic effects of the salts concerned.

The problem of salt accumulation in plants is not adequately comprehended apart from its inter-relations with the mechanism of oxidative breakdown of sugar and of the synthesis of protein which also requires oxygen. The nature of the bio-chemical link between these three apparently diverse processes, must elucidate all. From the previous stress on the importance of the ability of cells to grow the active participation of the processes of protein synthesis in salt uptake is not unexpected. This aspect of metabolism will no doubt figure prominently in future work on respiration and salt accumulation. Meanwhile the process of salt accumulation cannot be regarded merely as an equilibrium at a membrane endowed with special permeability properties. The living protoplast must intervene by aerobic metabolic processes which release energy and so determine the activity of the system with respect to salt uptake and all other processes which involve energy expenditure. Until the biochemistry of the process is known further speculation seems unprofitable.

*Birkbeck College,
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GENERAL DISCUSSION.*

Dr. J. F. Danielli (*London*) (*communicated*): Has Professor Collander made any temperature coefficient measurements on his plant cells?

Professor Kurt H. Meyer (*Genthod Geneve*) said: I would recommend to Professor Collander the use of oleyl alcohol as model substance, which

²⁸ Raper, H. S., *Physiol. Rev.*, 1928, 8, 245.

²⁹ Happold and Raper, H. S., *Biochem. J.*, 1925, 19, 23.

³⁰ Pugh, C. E. M., and Raper, H. S., *Biochem. J.*, 1927, 21, 1370.

* On 5 preceding papers.

in its solubility resembles the cell-lipoids much more closely than does oleic acid ester.

I would like to point out a few well-known facts which show the connection between lipid-solubility and surface-activity.

The distribution of a substance at equilibrium between an aqueous phase, a non-aqueous phase (*e.g.*, a lipid phase) and the boundary surface (adsorption layer), is determined by the energy content of the substance in the phase in question, E , and the integral of state, ϕ , (phase-volume) according to the following equation

$$N_w : N_{oil} : N_{ads.} = e^{-\frac{E_w}{RT}} \cdot \phi_w : e^{-\frac{E_{oil}}{RT}} \cdot \phi_{oil} : e^{-\frac{E_{ads.}}{RT}} \cdot \phi_{ads.}$$

where N_w , $N_{ads.}$, and N_{oil} represent the N_w = number of molecules in the aqueous phase, the adsorbed layer, and the non-aqueous phase, respectively, and ϕ_w , $\phi_{ads.}$, ϕ_{oil} = the corresponding phase volumes. The phase volumes are here proportional to the space available for the vibration of the molecules; this is considerably greater in the bulk liquid phase than in the boundary layer, which has only the thickness of one molecule.

From the equation the importance of the heat of solution or heat of adsorption can be seen. ($E_w - E_{oil}$ is the difference between the heats of solution in oil and water, $E_w - E_{ads.}$ is the heat of adsorption from the aqueous phase, etc.). Since $\phi_{ads.}$ is extremely small in comparison with ϕ_w and ϕ_{oil} , accumulation in the boundary layer, *i.e.*, adsorption can only occur if the heat of adsorption is large.

With regard to heats of solution and adsorption the following facts are known. Apolar substances (such as hydrocarbons, CS_2 , CCl_4 , etc.) have a larger heat of solution in lipoids than in water; substances with dipole groups, *e.g.*, $-OH$, $>C=O$, $-COOH$ or $-COO^-$ groups behave in the opposite way. A large heat of adsorption at the oil-water boundary is only shown by substances which have molecules with both water- and oil-soluble parts, so that, in adsorption, the heat of solution of the water-soluble and fat-soluble regions is set free as heat of adsorption and exceeds both individual heats of solution. In agreement with this fact we find that only substances such as alcohols, phenols, sulphonic acids, etc., pass to the boundary phase. Apolar substances such as CCl_4 , CS_2 and hydrocarbons (which are freely soluble in lipoids) or substances which contain only hydrophilic groups such as sugars (freely soluble in waters) are not adsorbed. If in a polar substance the fat-solubility predominates (higher fatty acids, higher alcohols) the solubility in water will be very slight or zero, but on the other hand the substance will be soluble in oil and will be adsorbed at the water/hydrocarbon boundary. If on the other hand the solubility in water predominates the substance may be insoluble in lipoids although the adsorbability remains—as in the case of the glucosides, which are rich in hydroxyl groups.

It seemed to me worth while to point out these relationships since they must be taken into account in all sorts of biological problems.

Mr. O. Gatty (*Cambridge*) said: Much reference has been made to the accumulation of potassium in terms of mosaic membranes; also to the relationship of oxygen uptake to potassium accumulation. Fresh evidence on both these points is now available in the case of frog skin.

Applying constant depolarising currents of 30 μ -amps. cm.⁻² the frog skin potential changes, largely owing to the operation of Ohm's law, but the time potential curve shows "a recession giving a cusped rather than asymptotic time course,"¹ It is doubtful whether this phenomenon can be interpreted in terms of a surface consisting only of one surface field. Spooner and Gatty² have observed similar cusped curves during the anodic polarisation of copper in aerated solution and interpret it in terms of two fields (one of metallic copper and the other of copper oxide), both

¹ See Dr. Blinks' paper 11, p. 991, for a similar effect with plant cells.

² See p. 104.

fields occurring in the solution metal interphase. An alternative explanation in the case of frog skin assumes the existence of two or more electric potentials, in series, as they occur at different levels in the skin. This evidence, therefore, indicates a multiplicity of electrically active surface fields, though they need not necessarily be lying side by side on the membrane of a single cell.

The first part of this cusped time-potential curve corresponds to an increase in ohmic resistance; this is inferred from preliminary experiments using an interrupted depolarising current maintained constant at 30 μ -amps. cm^{-2} after the first 10^{-8} sec. The potential under zero current does not alter sensibly once any initial effect due to depolarisation has occurred; during this time, however, the first part of the cusp is being traced out under depolarising current. The increase in resistance can probably be explained in terms of concentration polarisation where an ion of high mobility is electrolysed away from a region where the other ions have a lower mobility. This concentration polarisation corresponds to the "stimulations" discussed by Dr. Blinks and to the stimulation of nerve, except that nerve shows higher electrical resistance (*i.e.*, lower permeability) at zero density of polarising current while for frog skin the converse is true. The concentration polarisation effect is destroyed by cyanide but only after subsequent application of depolarising current, and not by p_{H6} . Replacing the sodium in Ringer by potassium till the potassium concentration is increased five-fold, also destroys the concentration polarisation effect. At greater potassium concentration (ten-fold or more) the electrical resistance of the skin is lowered; on adding M/500 cyanide in 10-K⁺ Ringer, the "concentration-polarisation effect" which had been destroyed reappeared, subsequently to disappear owing to the presence of cyanide. Moreover the decrease in electrical conductance of the skin due to adding cyanide was greater than in normal Ringer; the corresponding decrease in normal Ringer at p_{H6} is less than at p_{H8} .

These facts demonstrate a direct relationship between the effects due to potassium and those due to a marked respiratory inhibitor (cyanide). They suggest that a cyanide sensitive respiratory process produces an ion of relatively high mobility in the electrically active parts of frog skin. The concentration polarisation "effect" would be due to the electrolysis of this respiratory ion away from certain regions and this explains the observed increase in resistance. In the presence of potassium-rich Ringer solution the mobilities of other anions become increased relatively more than that of the respiratory ion. Thus relatively less current is carried by this ion and the concentration polarisation effect disappears. Cyanide, however, cuts off the supply of respiratory ion so that a much lesser current density can produce concentration polarisation of this ion, and once the concentration polarisation has been produced the respiratory ion is removed and no further concentration polarisation can be observed on subsequent depolarisations. The effect of M/500 cyanide and p_{H6} on the resistance would appear to be due largely to decreasing the anion permeability of the skin, just as potassium tends to increase its anion permeability, in order to explain the interaction of cyanide and potassium on resistance and that of cyanide and p_{H6} on the resistance.

Mrs. M. M. Brooks (*Berkeley*), in introducing Professor Brooks' paper, said: In the past, emphasis has been laid on the ratio of concentrations of certain ions in the external solution as compared with those in the sap of plants like *Valonia* and *Nitella*. The theories to account for the diffusion of ions apparently against the concentration gradient have dealt with the differences in concentrations of these two solutions. The present paper has endeavoured to show that there is at first a considerable concentration of the ions discussed in these experiments, in the *protoplasm* before they appear in the sap.

In the case of the penetration of radioactive K⁺ into *Nitella*, where it is possible to separate wall, protoplasm, and sap, and measure the

concentration in each separately, considerable accumulation was found in the *protoplasm*. For example, the few preliminary results which were roughly quantitative, comprised such figures as follows:

These figures represent results with comparable volumes of external solutions and sap. The wall and protoplasm of each sample were used without reference to volume or weight. This was always considerably less, however, than that of the sample of sap.

TABLE I.—No. of IMPACTS OF β -PARTICLES (NET VALUES).

Ext. Solution.	Wall.	Protoplasm.	Sap.
5	7	55	20

Dr. T. Teorell (*Uppsala*) said: In connection with the theory proposed by Professor Brooks (for ionic accumulation produced by an ionic exchange in the presence of a steadily supplied electrolyte), some questions may be asked:

(1) Why should it make a difference for the system as a whole whether the cations and anions strike the cell membrane side by side (distributed at random over the diffusion surface as in simple diffusion), or whether they strike through special areas, still molecular in size, assumed to be reserved for the ion species respectively?

There should be no difference between these systems when subjecting them to a quantitative treatment. I agree that an accumulation of K is likely to occur, but the main factor is the *difference in mobility of the H and HCO₃ ions*, belonging to the diffusing agent, H₂CO₃, which was supposed to be steadily produced. If the net charge of the membrane is zero, then it has been shown¹ that the accumulation ratio is determined by the following transcendental equation:

$$\log \frac{K_i}{K_o} = \frac{u_H - v_{HCO_3}}{u_H + v_{HCO_3}} \log \frac{H_i + K_i}{H_o + K_o},$$

where u_H and v_{HCO_3} denote the mobility *within* the membrane of the H and HCO₃ ions respectively. Let us assume that the relation $u_H : v_{HCO_3} = 5$ and $H_i = 10^{-8}$, $H_o = 10^{-8}$ and $K_o = 10^{-2}$; these figures may in their order of magnitude correspond to the biological conditions. Then it can be calculated that K_i becomes about 1.02×10^{-2} , i.e., *only about 2 per cent. accumulation* will appear. The reason is that the *absolute values* of the H ion concentration are very small (although the *ratio* $H_i : H_o$ is large).

Another difficulty is presented by the fact that the gradient of HCO₃ is directed *outwards*.²

A somewhat similar reasoning would probably be applicable if the membrane itself was of electrolyte character or otherwise possessed a positive or negative charge.³

(2) With regard to the suggestion that the protein molecules could actively transfer K and Cl, what forces could cause the protein-ion pair to migrate? How can it be shown that the positive protein-chloride and negative K-proteinate do not interact during their supposed journeys through the protoplasm?

(3) (*communicated*): In connection with the discussion of the K accumulation attention ought to be drawn to another dynamic principle, namely diffusion against a counter-current of water. A theory for such systems was first given by Hertz, who also utilised the principle for

¹ Cf. p. 983.

² In *Valonia* the ratio HCO₃_o : HCO₃_i is 1.58 according to Osterhout and Dorcas, *J. Gen. Physiol.*, 1925, 9, 255.

³ Cf. p. 1054.

separation of components in gas mixtures. Suppose we have two substances A and B which, due to some force, migrate from left to right. If A has a higher "mobility" than B, there will be a higher concentration ratio A/B to the right. If the *medium* (the solvent as a whole) also is moving, but in the opposite direction from the right to the left, the separation effect will be greatly amplified. Hertz showed that the ratio A/B is dependent not only on the mobilities but also on the velocity of the counter flow and the thickness of the diffusion layer (the membrane). If one could imagine a constant stream of water from the cells to their environment the Hertz principle would be applicable and the differences in K and Na ratios inside and outside can perhaps be explained. However, this suggestion does not account for the movement of K or Na into the cells against concentration gradients. If water was constantly streaming out of the cells, it had also to enter them somewhere. From this arises a difficult problem.

In general, it can be said that not much evidence is available as to the forces responsible for water migration in living systems. Osmotic and hydrostatic gradients seem not to be the only factors.

Professor Ancel Keys (*Rochester, Minn.*) said: A major difference between artificial membranes and the more important animal membranes is in the thickness. Collodion membranes are seldom less than 100 microns in thickness and permeable collodion membranes less than 50 microns thick have practically never been studied. Naturally a wall of even 50 μ will permit Helmholtz double layers of relatively high potential to be developed at both surface boundaries of the membrane. The membranes of the capillary wall, the alveolus of the lung, the villus of the intestine, etc., are so very much thinner—of the order of at most, a very few microns—that it seems doubtful whether they are comparable. Certainly Teorell's postulates cannot apply to the plasma membranes of cells which probably consist at most of only a few molecules in thickness. Furthermore, most of those animal membranes which may be thick enough to come within Teorell's scheme have the complication that the thickness is made up of living, *i.e.*, metabolising, cell substance. Surely this is a significant fact which must give one pause in translating concepts from collodion systems to biological systems.

Dr. T. Teorell (*Uppsala*), in reply to Professor Keys' remark (*communicated*): Some of Professor Keys' objections are quite sound if we consider purely *abstract* systems. The limitations of the scheme I have presented are the same as those of the Nernst-Planck theories for diffusion potentials in general: When one deals with boundary layers (or membranes) with a thickness of the order of distances between the solute molecules, then the concept of concentration gradients loses its usual meaning and the theories as formulated break down. Planck¹ states expressively that *die ganze Theorie auf der räumlichen Stetigkeit der Konzentrationen aufgebaut ist*. Planck calculates that the lower limit of applicability for a N/1000 solution is 10^{-6} cm. (100 Å.). With higher concentrations, such as found in physiological systems, this limiting value of a membrane thickness becomes still smaller. The figure 100 Å. corresponds to 2-4 layers of lipid molecules. The thickness of all sorts of epithelial membranes as capillary walls, etc., are far above this figure.

Furthermore, the concept of a plasma membrane being only a few molecules thick is more of a "morphological" significance than of functional: if the actual membrane consisted only of a monolayer, its "effective" thickness (in regard to the effect on diffusion across it) is very much greater, owing to the presence of "unstirred layers" of the surrounding solutions, one layer on each side of the membrane (in spite of convection currents). These "unstirred layers" are bound to exist due to pure hydrodynamical reasons. Working on plain, very thin cellophane membranes I have found

¹ *Z. Physik*, 1935, 94, 469.

that the average thickness of the "unstirred layer" was around 0.03 millimeter even at a very vigorous stirring of the bulk solutions. Dr. Schulman and I have recently found that there exists a rigid layer of the aqueous solution underneath monomolecular films. Also in cases where there was an intensive convection the bulk phase relative to the film, the mean thickness¹ of the rigid, adhering layer of aqueous solution was of the order 20-30 μ . These observations suggest that the *effective* thickness of biological diffusion layers can hardly be less than a few microns.

I feel therefore that Professor Keys is unjustified in hesitating to apply analogies from "collodion systems" to biological systems, at least as far as physical phenomena are concerned.

Mr. G. S. Hartley (London) said: In Thover's experiments on *diffusion rétrograde*, a solute, initially present at uniform concentration, can be caused to diffuse temporarily if a second diffusible solute is introduced. As a result, a concentration gradient is *built up* and diffusion must occur, during part of the experiment, from a lower to a higher concentration. Just as in the experiments Dr. Teorell has described, it is possible to arrange that the second solute diffuse steadily *through* a layer of the original solution, thus establishing a steady gradient of concentration of the first solute.² In such a system both ions of an electrolyte may be permanently at a higher concentration in one part of a system than in another, whereas in Dr. Teorell's experiments³ the gradients of the cations and anions of the non-diffusing electrolytes must be of opposite sign.

While both types of *diffusion rétrograde*, particularly the ionic redistribution described by Dr. Teorell,³ may play an important part in vital processes, some cases of salt accumulation by cells, as for example the very striking ones described by Dr. Steward, seem to require a very different driving mechanism. While I agree with Professor Krogh's contention that the driving force should be sharply differentiated from the true membrane function, I think it is useful to enquire into what driving mechanisms are available. The answer may suggest what to look for in membranes proper. It is necessary first to point out a fundamental difference between Thover's *diffusion rétrograde* and the accumulation of salt in living cells. In the former the "retrogression" is only in concentration. A solute may diffuse from a lower to a higher concentration under the influence of a second solute, but it does so⁴ only because the second solute increases its chemical potential (lowers its solubility). A sufficient concentration of acetone will throw potassium chlorate out of a solution in water: a smaller concentration, introduced in one part, will cause the salt to diffuse away from this part to the parts less concentrated in acetone. From the *thermodynamic* point of view there is nothing "retrograde" about the process.⁴ It is quite otherwise with the accumulation of salts inside cells. The concentration of various products of metabolism will be greater inside the cell than out. Whatever the nature

¹ Unpublished results.

² Hartley, *Trans. Faraday Soc.*, 1931, **27**, 10.

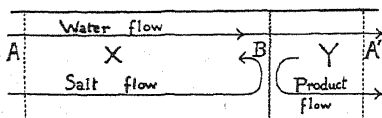
³ Teorell, *Proc. Nat. Acad. Sci. Wash.*, 1935, **21**, 152; *J. Gen. Physiol.*, 1937, in press.

⁴ It can easily be shown⁵ that complete thermodynamic equilibrium cannot be attained in regard to *both* non-diffusing components (solvent and first solute) even in the steady state, as long as the second solute is allowed to diffuse. We shall not, therefore, in general, have complete equilibrium of *either*. This constitutes a slight correction to the excellent theoretical treatment of the ionic distribution case by Dr. Teorell,⁵ but one of only very minor importance in dilute solutions. In the more concentrated solutions that I examined,² using one non-electrolyte solute, equilibrium appears to be nearly approached for the non-diffusing solute. This is due to the diffusing solute having a very much greater effect on the chemical potential of the non-diffusing solute than on the water, as is generally the case.

⁵ Teorell, *Proc. Nat. Acad. Sci.*, 1935, **21**, 152 (in particular (c), p. 156).

of these products, they are certain not to be such as will increase considerably the solubility of simple "inorganic" salts, and are much more likely to have, like acetone, the reverse effect. The observed excess concentration of salt inside the cell requires therefore that its *chemical potential* be higher inside the cell, and the salt must be accumulated *against* this potential gradient. No type of simple diffusion can explain this. If one membrane permits both the salt and the products of metabolism to go through, they will go through in the *same direction*. The apparently inevitable conclusion, on which I should like the opinion of other physical chemists, is that *more than one kind of membrane* (in the widest sense) must be involved. It is only too easy to invent models of biological processes with very little evidence as to their relevance, but I hope I may be excused for putting forward a generalised model of how, by the use of more than one membrane, salt accumulation may be brought about by the normal dilution of some other substance.

Suppose for simplicity that the outer membranes AA' are permeable to everything, being membranes only in the sense that they prevent convection. Let the cell be divided by a membrane B, permeable, in the simplest case, to water only. Let a diffusible product be produced by some vital process in the compartment Y. If this product is present in sufficient concentration, water will be abstracted through B from the compartment X. This water will be replaced through A by external solution. Water will thus flow *through* the cell in the direction of the long arrow, the salts in the external solution will pass into X through A along with the water, but will be filtered out by B and accumulate in X. It is to be noted that they do not accumulate by diffusion but by



filtration: diffusion through A will tend to reduce the accumulation. Meanwhile, the products of metabolism will flow out with the water, and partly by diffusion also, through A'. The process would, in an ideally efficient system of this type, go on until the osmotic

pressure in X reached that in Y. The more diffusion occurs through A and A' the less efficient the system and the greater the rate of metabolism necessary to maintain the salt accumulation.

I put forward this model only as a positive supplement to my previous negative conclusions. There could be an infinite number of variations on the principle: the parts might have a great variety of shapes and sizes: other membranes could be introduced, and if selective membranes were present we could explain selective accumulation. The essential point, if my argument is sound, is that the thing cannot be done with one kind of membrane only, but can be done very simply if we have at least two. Have the physiologists any evidence bearing on this conclusion?

Professor J. H. Gaddum (London) (communicated): It is surprising that Dr. Hartley should have invented a model which is very like what is found in the mammalian kidney. The membrane A is the glomerulus which filters water and small molecules from the blood. X is the lumen of the renal tubules and Y is one of the cells lining the lumen. Metabolic changes occur in Y which lead to a reabsorption of water and certain other substances which are then returned to the blood. Actual kidneys are more complex than this, but Dr. Hartley's mechanism does seem to play an important part in their activity.

Professor A. Krogh (Copenhagen) (communicated): While I agree heartily in the conclusion that the accumulation described is a vital process involving energy I believe that the growth factor has been over-emphasised. It is the natural function of roots to absorb salts (and water) from solutions which are (and in order not to kill the roots indeed must be) very dilute, and the salts are not only concentrated in cells, but transported

across cells to the sap which rises in the stem. When the process is studied on roots the necessity for growth is not conspicuous as the absorption is certainly not confined to the growing tips of the roots. I think Lundegårdh has shown in his latest paper that anions only are taken up by the active process, involving a definite rate of metabolism over and above the basal which is necessary for maintaining the life of the tissue.

Dr. F. C. Steward (*London*) said with regard to Mrs. Brooks' remarks: There are two aspects which require careful consideration. (1) The suggestion that the protoplasm is the seat of the initial accumulation, and (2) the modified form of the earlier ionic exchange theory.

The active participation of the living protoplasm in salt accumulation by cells, because the process is linked with metabolic processes, is now beyond all reasonable doubt. Clearly, however, no sharp line can be drawn between accumulation in the protoplasm and accumulation in the sap. Admittedly the contrast between these phases is unusually distinct in the vesicle of *Valonia* but even in this case, and if the evidence of accumulation in the protoplasm is conclusive, it would be difficult to maintain that the protoplasm is not minutely vacuolate. Accumulation in the protoplasm, therefore, means accumulation in vacuoles in more intimate association with the protoplasm than the very large sap-filled cavity of the *Valonia* vesicle—a cavity which is actually more analogous to a fluid surrounded by a sheath of cells than one within a vacuole within a single protoplast.

Only two comments are necessary to deprive the hypothetical suggested mechanism of all claim and to explain the general facts of salt accumulation. Firstly, the mechanism, like its predecessor, still depends upon a gradient of $[H^+]$ and demands that cells should respond to changes of $[H^+]$ in a manner which *Nitella*, roots, storage tissues and even *Valonia* do not fulfil. Secondly, the mechanism evades the necessity for *oxidation* which is of even more importance than the production of carbon dioxide. At best it represents a possible mode of entry but does not in any way explain the facts of accumulation.

Professor R. Collander (*Helsingfors*), in reply (*communicated*): A study of the temperature coefficient of permeation was started some time ago at the botanical laboratory of Helsingfors. The Q_{10} -values so far found lie between about 2 and 3, but it does not seem impossible that lower or higher values may be found when the study is extended to other substances than those hitherto used (glycerole, urea).

The replies of **Professor Blinks**, **Professor Osterhout** and **Mrs. Brooks** will be inserted later if received before going to press.

THE RESTING POTENTIALS OF MUSCLE AND NERVE, AND DEPOLARISATION BY VARIOUS AGENCIES.

BY S. L. COWAN.*

Received 3rd March, 1937.

When two non-polarisable electrodes are placed in contact with two points on the longitudinal axis of an uninjured resting nerve trunk or muscle no potential difference can be detected—the outside surface: uniform. If, however, the tissue beneath one of the electrodes is injured then a potential difference is found between the injured and uninjured points. Usually this potential difference, the “resting” or “injury”

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potential, is of the order of tens of millivolts, and the direction of current flow in the external circuit indicates that the injured region is negative relative to the uninjured region. A nerve trunk or a muscle comprises a bundle of small units lying parallel to one another—nerve fibres or muscle fibres. Each fibre is bounded by a membrane, and apparently injury at one point permits connection to be made to the inner side of this membrane. The injury potential is then the resultant of the potentials of all the component fibres, which may be regarded as being connected in parallel, partly short-circuited by the tissue fluids normally present between the fibres.

From the experimental evidence available it seems that the membranes bounding muscle fibres and nerve fibres are polarised ones permeable to small cations, such as K^+ and H^+ , and little if at all permeable to larger cations, such as sodium, and to anions. As a first approximation the injury potential has been treated as a diffusion potential due to the constraining influence of the membrane on certain ions, although, as Teorell¹ has pointed out, this involves disregard of phase-boundary potentials, not always negligible, at the two surfaces of the membrane. With the same binary electrolyte present in concentrations c_1 and c_2 on the opposite sides of a negatively charged membrane the principal potential is the diffusion potential

$$E = \frac{u-v}{u+v} \cdot \frac{RT}{F} \log \frac{c_1}{c_2}$$

where u and v are the mobilities of the cation and anion respectively within the membrane. In the limit, when the membrane becomes impermeable to anions, the potential becomes

$$E = \frac{RT}{F} \log \frac{c_1}{c_2}$$

In accordance with the above conception of the injury potential, both in muscle² and in nerve,³ the magnitude of the injury potential has been found proportional to the absolute temperature of the uninjured region of the tissue and independent of the temperature of the injured region. Departures from this proportionality have been recorded for muscle and for nerve and explained as due to secondary factors.⁴

Macdonald⁵ was the first to examine the effects of alteration of the ionic composition of the fluid bathing the exterior of the nerve trunk upon the injury potential. He made experiments on frog's medullated nerve with NaOH, HCl, KCl and NaCl solutions. Over a concentration range $\frac{1}{2}$ to 1 molar he found a nearly linear relation between the injury potential and the logarithm of the potassium salt concentration in the solution bathing the nerve trunk; also he showed qualitatively that potassium was the chief cation present in the nerves. Macdonald concluded that the injury potential of nerve is a diffusion potential between a concentrated potassium salt solution within the fibre and a more dilute potassium salt solution surrounding the fibre and that these solutions are separated by a non-aqueous membrane.

¹ Teorell, T., *Proc. Soc. exp. Biol. Med. N.Y.*, 1935, **33**, 282.

² (a) Adrian, E. D., *J. Physiol.*, 1924, **59**, 1P. (b) Bernstein, J., *Pflüger's Arch.*, 1897, **67**, 349.

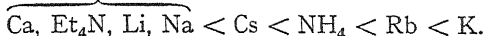
³ (a) Bernstein, J., *Pflüger's Arch.*, 1902, **92**, 521. (b) Kolb, H., *Z. Biol.*, 1928, **88**, 47.

⁴ For references see Gerard, R. W., *Physiol. Rev.*, 1932, **12**, 469 at page 510.

⁵ Macdonald, J. S., *Reports of the Thompson Yates Laboratory, Liverpool*, 1902, **4**, 213; *Proc. Roy. Soc., B*, 1905, **76**, 322.

With frog muscle Höber⁶ found that cations influenced the resting potential in the following order of effectiveness: $\text{Li} < \text{Na} < \text{Mg} < \text{Cs} < \text{NH}_4 < \text{Rb} < \text{K}$. Anions also influenced the potential to a lesser degree, and he arranged them in the order: $\text{CNS} < \text{NO}_3 < \text{I} < \text{Br} < \text{Cl} < \text{acetate} < \text{HPO}_4 < \text{SO}_4$.

More recently Netter⁷ observed that the resting potential of frog nerve was independent of the species or valency of the anions present in the external solution, whilst cations were effective in the following order:



He suggested that if the membrane were regarded as an ionic sieve, analogous to the negatively charged collodion membranes of Michaelis,⁸ then the order of effectiveness of the cations was not very different from the order of penetration which might have been expected as a consequence of their ionic volumes, namely: $\text{Li} < \text{Na} < \text{NH}_4 < \text{K} < \text{Rb} < \text{Cs}$. The deviations from the expected positions in the series he attributed to an action of the ions concerned upon the membrane—they might produce a change of pore size or of charge. Similar conclusions were reached by Höber and Strohe.⁹

Since sodium, potassium and calcium are the only cations ordinarily present in considerable amounts in muscle and nerve we can conclude that the resting potentials of these tissues are mainly governed by the potassium ion concentration. There then arises the question whether the potassium ion concentration within the tissue is sufficient to account for the size of the observed potential. From the analyses of frog muscle by Hegnauer, Fenn and Cobb¹⁰ the concentration of potassium within the fibres is calculated to be about eighteen times that in the fluid surrounding them. The experiments of Hill and Kupalov¹¹ on the osmotic pressure of frog muscle show that only a negligibly small fraction of the potassium within the fibres could be osmotically inactive, likewise measurements of the internal conductivity of frog muscle fibres¹² indicate that there are no unionised potassium compounds with the cell. Therefore the potential to be expected is 73 millivolts. The potential observed was 41.6 millivolts. In crab's non-medullated nerve Cowan¹³ found an approximately linear relation between the injury potential and the logarithm of the potassium concentration in the solution bathing the fibres. Sodium ions and different anions affected the potential little. Analyses showed that the potassium concentration within the fibres was at least thirteen times as great as in the external fluid usually bathing the fibres. There is evidence, although of a rather less direct nature than in the case of frog muscle, that only a very small fraction of the potassium present in the fibres can be in an unionised state.^{13, 14} The injury potential observed was about 30 millivolts, whilst the calculated value is about 66 millivolts. Thus both in muscle and nerve the observed injury potential is less than that calculated from the ratio $(K_{\text{inside}})/(K_{\text{outside}})$.

⁶ Höber, R., *Pflüger's Arch.*, 1905, **106**, 599.

⁷ Netter, H., *Pflüger's Arch.*, 1927, **218**, 310.

⁸ Michaelis, L., *J. gén. Physiol.*, 1925, **8**, 33.

⁹ Höber, R., and Strohe, H., *Pflüger's Arch.*, 1929, **222**, 71.

¹⁰ Hegnauer, A. H., Fenn, W. O., Cobb, D. M., *J. cell. comp. Physiol.*, 1934, **4**, 595.

¹¹ Hill, A. V., and Kupalov, P. S., *Proc. Roy. Soc., B*, 1930, **106**, 445.

¹² Bozler, E., and Cole, K. S., *J. cell. comp. Physiol.*, 1935, **6**, 229.

¹³ Cowan, S. L., *Proc. Roy. Soc., B*, 1934, **115**, 216.

¹⁴ Beresina, M., and Feng, T. P., *J. Physiol.*, 1933, **77**, 111.

The discrepancy has been attributed to short circuiting by connective tissue and by the solution between the fibres (but see Teorell).¹

The above description of the injury potential only applies to resting tissues supplied with oxygen. If nerve be asphyxiated the injury potential diminishes, and the change is reversible if not carried too far.^{13, 15} In Gerard's experiments this diminution took place only when the intact region was asphyxiated and not when the injured region was asphyxiated. It appears that part of the oxidative work done by the cell goes to maintain the normal impermeability of the surface. If this conclusion is taken at its face value it might be said that the principle of Le Chatelier applies to muscle, for if the injury potential be reduced by potassium ions then the oxygen consumption is increased.¹⁰ Like potassium acetylcholine depolarises muscle¹⁶ and the concentration required to produce a given effect is about one-hundredth of the potassium concentration required to produce the same effect. Nachmansohn¹⁷ has shown that to produce a given increment in the oxygen consumption of muscle acetylcholine is effective in about a fiftieth of the dose in which potassium is.

When a muscle or nerve is excited one of the manifestations of activity is a propagated wave of electrical change that passes along the surface of the fibre. If a non-polarisable electrode is placed on an injured region and another electrode on an intact region, then as the disturbance passes beneath the electrode on the intact surface the injury potential diminishes temporarily—this is the "action potential," or "negative variation of the injury current" of the classical physiologists. Undoubtedly this action potential is complex. On the one hand Gasser and his colleagues¹⁸ reported that in frog nerve at room temperature the first part of the action potential, the "spike," attained its maximum in less than 3/10,000 of a second and then began to fall rapidly; after a short time there was a discontinuity and the potential fell more slowly than before. This latter part of the response, the "after-potential," could be suppressed by oxygen want or by the action of carbon monoxide in the dark. On the other hand in crab's non-medullated nerve the "after-potential" following the spike was very pronounced¹⁹ and oxygen want lengthened its duration.^{15b} Furusawa's finding has been confirmed by Cowan and Feng.²⁰ The spike is the initial excitatory process common to both tissues, and the disturbance of immediate interest for the purposes of this paper. The after-potential is connected with an oxidative recovery process following excitation and appears to differ in the two kinds of nerve.

Chemical studies of muscle²¹ and of frog's medullated nerve²² like the electrical ones lead to the conclusion that the membranes in both tissues are permeable to cations, such as K^+ and H^+ , but not to large cations, such as Na^+ , or to anions. The nature of the membrane is unknown. Höber²³ has recently discussed the merits of three possibilities:

¹⁵ (a) Gerard, R. W., *Amer. J. Physiol.*, 1930, **92**, 498. (b) Furusawa, K., *J. Physiol.*, 1929, **67**, 325.

¹⁶ Cowan, S. L., *J. Physiol.*, 1936, **88**, 3P.

¹⁷ Nachmansohn, D., *Personal communication*, 1937.

¹⁸ Gasser, H., *Occasional Publication of the American Association for the Advancement of Science*, No. 2, Supplement to *Science*, 79.

¹⁹ Levin, A., *J. Physiol.*, 1927, **63**, 113.

²⁰ Cowan, S. L., and Feng, T. P. (Reported in ¹⁴), 1933.

²¹ (a) Mond, R., and Netter, H., *Pflüger's Arch.*, 1930, **224**, 702; 1932, **230**, 242. (b) Fenn, W. O., *Physiol. Rev.*, 1936, **16**, 450.

²² Fenn, W. O., Cobb, D. M., Hegnauer, A. H., Marsh, B. S., *Amer. J. Physiol.*, 1934, **110**, 74.

²³ Höber, R., *Physiol. Rev.*, 1936, **16**, 52.

a sieve-like membrane;⁸ a layer of water immiscible material, such as lipid;²⁴ a surface film.²⁵ Whichever of these it may be, there is evidence that in a large number of biological materials,²⁶ including muscle and nerve, the properties of the membrane are very considerably affected by ions to which it is not permeable, *e.g.*, Solandt²⁷ has found that calcium ions increase the speed of "accommodation"²⁸ in nerve. Alteration of the charge on a membrane might alter its polarisability by altering its permeability to ions of a certain size. From measurements of the impedance of muscle over a wide range of frequencies Bozler and Cole¹² have concluded that the capacity across the membrane is a polarisation capacity, not a static capacity like that of the membrane of the red blood cell.²⁹

The spike of the action potential implies a current in the opposite direction to that of the injury potential. This might be brought about by a temporary increase in the permeability of the tissue membrane to larger cations or even to anions. Dubuisson³⁰ has reported that excitation produces a decrease in the impedance of muscle, whereas Bozler³¹ has reported an increase. Cloetta³² has found a loss of potassium from stimulated muscle and Cowan¹³ a loss of potassium from stimulated crab nerve, but Netter and Mond^{21a} have been unable to find any loss of potassium from stimulated frog muscle. From measurements of the heat production in frog nerve Hill³³ has calculated that the heat per isolated impulse per gram of nerve is 2.2×10^{-7} calories at 0° C. and 1.1×10^{-8} calories at 30° C. He has calculated that these amounts of heat correspond to 5×10^{-3} and 2.5×10^{-4} erg per cm.² of nerve fibre surface. Further, if it is assumed that the nerve surface is covered with a unimolecular condensed film composed of molecules each of 25×10^{-16} cm.² cross-sectional area, then the energy corresponds to 0.18 and 0.009 calorie per gram molecule of molecules on the surface. Thus, the surface energy corresponding to the heat production of nerve is calculated to be less than 1/4000 of that of an olive oil-water interface. Hill has pointed out that these figures seem to preclude, at least in nerve, anything so drastic as the breakdown of a unimolecular condensed film. However, it is not necessary to postulate a breakdown—the mere alteration of the charge on a very thin film might increase the effective diameter of the "pores" sufficiently to permit the passage of certain ions that could not pass through the "resting" or normally charged film. In the case of nerve excitation by our electrical stimulus might be pictured in the following way. At the cathode the applied current might remove certain cations normally oriented at the outer surface of the membrane and responsible for its low permeability to other ions. The increase of permeability would then permit a discharge of the potential normally present across the film—the injury potential.

²⁴ Beutner, R., *Die Entstehung Elektrischer Ströme in Lebenden Geweben* (Stuttgart, 1920); *Physical Chemistry of Living Tissues and Life Processes* (London, 1933).

²⁵ Danielli, J. F., *J. cell. comp. Physiol.*, 1936, **7**, 393.

²⁶ See Lillie, R. S., *Protoplasmic Action and Nervous Action*, London, 1923.

²⁷ Solandt, D. Y., *Proc. Roy. Soc., B*, 1936, **119**, 355.

²⁸ Hill, A. V., *Proc. Roy. Soc., B*, 1936, **119**, 305.

²⁹ Fricke, H., and Morse, S., *J. gen. Physiol.*, 1925, **9**, 153.

³⁰ Dubuisson, M., *Arch. Int. Physiol.*, 1934, **38**, 85.

³¹ Bozler, E., *J. cell. comp. Physiol.*, 1935, **6**, 217.

³² Cloetta, M., Fischer, H., and van der Loeff, M. R., *Arch. exp. Path. Pharmacol.*, 1934, **174**, 589.

³³ Hill, A. V., *Chemical Wave Transmission in Nerve*, Camb. Univ. Press, 1932.

The discharge of the injury potential might, in its turn, disturb the permeability-controlling cations at adjacent parts of the outer surface of the film and permit a further discharge of the injury potential at those points. In this way the permeability change and the subsequent discharge of the injury potential might traverse the length of the cylindrical membrane bounding a nerve fibre. At the anode the applied current would not remove but add to the cations oriented at the outer surface of the membrane.

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THE PHYSICO-CHEMICAL BASIS OF ELECTROTONUS.

By H. ROSENBERG (*London*).

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I. Fundamental Experiments in Nerve.

When an electric current is passed longitudinally through a section of a nerve the current lines show a peculiar distribution. In addition to the current flow through the interpolar stretch between the contact points of the electrodes, the current spreads laterally through the extrapolar regions. This phenomenon is called physical electrotonus.¹ A galvanometer connected with two extrapolar points of the nerve surface lateral from anode or cathode indicates a current which, on either side, has the opposite direction to the interpolar flow (see Fig. 1). In the extrapolar region a longitudinal potential gradient (anodic or cathodic) is established which declines exponentially along the nerve. If we call P_0 the electrotonic potential at the pole and x the intermediate distance between this pole and an adjacent point (the far end of the nerve taken as relative zero) the potential of this point

$$P = P_0 e^{-\alpha x} \quad \dots \dots \dots (I)$$

This equation² holds if x is greater than 0.2—0.3 cm. The constant α differs in various nerves and under certain conditions. When short constant current pulses of subliminal (*i.e.*, not stimulating) strength are employed, *e.g.*, 20 mV. for 10 msec., α is almost equal for the two polarities, for instance 1.68 and 1.62 in cat- and anelectrotonic conditions respectively (sciatic nerves of *R. temporaria* at room temperature).³ These are minimum values; after comparatively long durations of current flow α increases to about 3. This change is probably related to opposite changes of the intensities of an- and catelectrotonic currents during continuous passage of relatively strong currents.

II. Structure and Function in Nerve and Core-Conductor.

The current and potential distribution in nerve, therefore, is different from that in a cylindrical metallic or fluid conductor. It is, however,

¹ Du Bois-Reymond, E., *Untersuchungen über thierische Elektrizität*, 1843, II., 1, 289, Berlin.

² Weber, H., quoted from Hermann, *Handb.*, 1879, 2, 183.

³ Rosenberg, H., XIV. *Congr. int. Fisiol. Comunicaz.*, 1932, 220.

possible to produce similar phenomena in a suitable combination of inorganic materials which imitates the structure of nerve. The simplest assumption is that the physiological unit of nerve consists of an axon surrounded by a membrane and a fluid layer which is formed by the connective tissue. If we replace the axon by a wire (core) and the interstitial fluid by an envelope of electrolyte solution we obtain a so-called core-conductor.⁴ This model contains no "anatomical" membrane. Its correlate is the polarisable interface which exists in combinations as (1) Pt in ZnSO_4 solution or (2) Zn in NaCl solution. Hermann has demonstrated that, regarding "passive" electrical properties, the analogies between core-conductor model and nerve in steady state are complete. While combination (1) shows equal an- and catelectrotonus, combination (2) yields the same difference in favour of the anelectrotonus as the nerve. A nonpolarisable arrangement, e.g., Zn in ZnSO_4 solution does not exhibit any electrotonus.

The explanation is obvious. The main part of the current applied to the fluid envelope immediately passes to the metallic core. If the interface is non-polarisable the current enters and leaves the wire within a circumscribed polar region. If, however, polarisation develops at the boundary of envelope and core, the counter e.m.f. partially blocks the passage of the current underneath the electrodes; and if this apparent increase of transverse resistance is sufficiently great compared with the longitudinal resistance of the envelope, the current is diverted laterally according to the rate of polarisation. Hence in the extrapolar regions the current flows in opposite directions through core and envelope (the potential gradient along the envelope being measured). If the polarisation prevails at the anode, the anelectrotonus is stronger and extends further than the catelectrotonus, and vice versa. In agreement with this conception there is no electrotonic spread in model and nerve when a transverse current is applied.

A passive iron wire immersed in nitric acid has similar features.⁵ In spite of the physical correspondence realised in these models it seems preferable to approach biological conditions by substituting an organic membrane for polarisable interface or oxide film, and a fluid conductor of physiological composition for the metallic core.⁶ To this end Labes and Zain⁷ used collodion sacs which were filled with a neutral solution of potassium phosphate and placed separately in beakers containing 0.5M sodium chloride solution isotonic with the phosphate mixture. The inner solutions and also the outer solutions of a series of such cells were connected by means of glass capillaries filled with the respective solutions. The resistances of the capillaries between the outer fluids and of the membranes between inner and outer fluids were considerably higher than those of the inner capillaries. The membranes were not perfectly impermeable to anions (as the axon membrane is supposed to be),⁸ but slightly penetrable by chloride ions.

This discontinuous membrane core-conductor permits the determination of the potential distribution by measuring the potential differences between inner and outer fluid of each cell as well as between the inner

⁴ Matteucci, C., quoted from Hermann, *Handb. d. Physiol.*, 1879, 2, 174, Leipzig; Hermann, L., *Pflüger's Arch.*, 1872, 5, 264; 6, 312; 1873, 7, 301.

⁵ Lillie, R., *J. gen. Physiol.*, 1925, 7, 473.

⁶ See Boruttau, H., *Pflüger's Arch.*, 1901, 84, 309.

⁷ Labes, R. and Zain, H., *Arch. exp. Path. Pharmac.*, 1927, 126, 352.

⁸ Netter, H., *Pflüger's Arch.*, 1927, 218, 310.

and between the outer fluids of each adjacent pair. From these figures and the known resistances of the capillaries the intensities of the currents traversing capillaries and membranes were computed. The potential difference between "core" and "envelope" across the membrane was of the order of 90 mV. When a potential was applied to the outer fluids of the two central cells the current was not confined to these polar cells, but partly diverted through the extrapolar sections. The potential declined characteristically as the distance from the respective poles increased, anelectrotonus exceeding catelectrotonus in height and extent. Correspondingly the current through the membrane was greater at the cathode than at the anode and its decrease was steeper in the catelectrotonic than in the anelectrotonic region. Hence the ratio *membrane current : potential difference across membrane* was smaller on the anodic than on the cathodic side, and the difference of this penetration factor increased with the duration of current flow. At the same time the anelectrotonus rose and the catelectrotonus subsided.

With some simplifications the authors reduce this effect of the current to a transport of Na- and phosphate ions away from the membrane and of K- and Cl-ions towards the membrane at the cathodic region and vice versa at the anodic region. That is to say: in the cathodic membranes well-conducting ions increasingly replace poorly conducting ions whereas the opposite process occurs in the anodic membranes in which the phosphate ions may even obstruct the pores. The influence of such changes on the polarising current was shown in a similar (collodion tube) model: when the current was applied to one end of the inner fluid and to a localised area of the envelope the intensity depended on the direction of the current. When the local electrode was the cathode the intensity of the polarising current increased and the electrotonic current decreased whereas with local anode the conditions were inverted.⁹ These results are in accordance with those obtained in nerve when a current is led to an injured end (*i.e.*, without interference of membranes) and to an intact part of the surface.¹⁰

From this survey, which comprises only a selection of the details, it seems evident that the mechanism of the models is essentially related to the respective processes in nerve. Now we reverse the problem. Does the nerve reveal phenomena predicted by the theory which is derived from the physico-chemical conception? In this respect we have to consider that the model represents a single axon in its medium while the nerve is a complex of numerous heterogeneous fibres embedded in various sheaths of connective tissue. Unfortunately relevant experiments on single fibres are not reported.

III. Theory of the Core-Conductor.

It is conceivable that the theoretical treatment of the core-conductor meets with difficulties which necessitate simplifications. Cremer¹¹ succeeded in deriving a differential equation

$$\frac{\partial P}{\partial t} = a^2 \frac{\partial^2 P}{\partial x^2} - h^2 P \quad . \quad . \quad . \quad (2)$$

for the propagation of polarisation in a core-conductor with depolarisation (*e.g.*, the original model). Because of the analogy with the heat

⁹ Ebbecke, U., *Z. Biol.*, 1931, 91, 247.

¹⁰ Ebbecke, U., *Pflüger's Arch.*, 1922, 195, 555.

¹¹ Cremer, M., *Z. Biol.*, 1899, 37, 550.

equation he regarded the propagation of polarisation as similar to that of heat in a long cylindrical rod of small diameter. Another analogy is the charge of a cable (neglecting inductance). Cremer found¹² that at the polar cross-section (*i.e.*, for $x = 0$) the development of polarisation follows the probability integral $\phi(\sqrt{\tau})$. The general solution has not been published. Cremer admits that the integration involves many premises which theoretically are not fully justified and experimentally (in nerve) hardly realised. Hermann¹³ reverted to a resistance-capacity combination which he preferred for mathematical treatment and quantitative test. This replacement implies the idealisation that below the electrolysing potential a non-corrodable polarisation cell acts as a condenser of definite capacity. In such an electrode during application of a constant potential a small current is flowing, *i.e.*, the condenser has a leak. To a first approximation this cell is described by a fixed capacity c with a fixed resistance r in series and another resistance r_1 in parallel. From such elements Hermann composed a chain conductor in which one side of the connected condensers (AB) represents the envelope, the other side (CD) the core, while the resistances r_1 , parallel to the condensers c , represent the resistance across the interface between core and

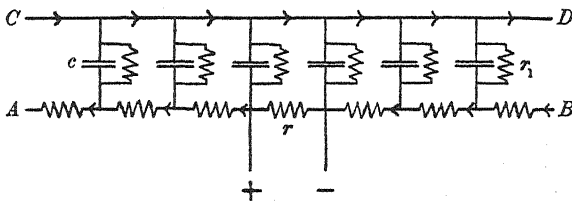


FIG. 1.—Scheme of a chain conductor with three fixed magnitudes c , r and r_1 (after Hermann). AB envelope, CD core. Polarising potential applied to two points of the envelope. Arrows indicate directions of current flow in core and envelope.

envelope (Fig. 1). Since in the wire-fluid model the core has a resistance substantially smaller than the envelope, Hermann apparently assumed it to be sufficient for a formal examination to concentrate the resistances of core and envelope in each link into one resistance r . In Cremer's opinion this simplification is inadmissible since in nerve both core and envelope possess high resistances. Supposing the nerve fibre to be so thin that the other dimensions may be neglected in comparison with the length, Hermann obtained a differential equation for this continuous linear capacity conductor with finite leak resistance (*i.e.*, with depolarisation) which is identical with Cremer's "heat" equation. In his notation P is the potential of the charge at the point x at time t ; the constants are defined by the values of r , r_1 and c per cm. (r_1 being inversely proportional to the length).

For the case of permanent application of a constant potential the integral for the extrapolar potential P was not solved by Hermann. It permits, however, the conclusion that the development of this potential begins at all points at the instant at which the polarising current starts to flow, but that the steepness of the rise gradually diminishes with increase in the distance from the pole. The electrotonic potential tends towards a final value which is the same for an- and catelectrotonus;

¹² Cremer, M., *Handb. d. norm. and path. Physiol.*, XVIII., 1932, 241, Berlin.

¹³ Hermann, L., *Pflüger's Arch.*, 1905, 109, 95.

when the stationary state is reached the electrotonic potential gradient is an exponential curve (as shown by eqn. (1) which follows from eqn. (2) if $t = \infty$). Since it is found that the electrotonic constant $\alpha = \sqrt{r/r_1}$ (per cm.), the steady electrotonus is conditioned by the transverse resistance r_1 and independent of the capacity c which only influences the rate of development. The magnitude of the steady electrotonus, therefore, does not depend directly on the polarisability, but on the boundary resistance caused by polarisation. An amalgamated zinc wire in ZnSO_4 solution exhibits no electrotonus because there is no such resistance, i.e., the extrapolar potential of the core theoretically equals zero. An "ideal" capacity conductor (without depolarisation) also shows no steady electrotonus since the extrapolar potential is everywhere the same as that of the electrode. It is unnecessary to discuss the effect of an inductance in the resistance r , since there is no experimental evidence in nerve for such an assumption.

IV. Recent Analysis of Electrotonus in Nerve.

Experiments on the electrotonic transients in nerve serve as a suitable test for some notable consequences of these theoretical considerations. Exact data on these points are almost exclusively due to recent technical improvements (amplifier and oscillograph). We can, therefore, disregard previous controversial statements which are reconciled by the new results.¹⁴ The following presentation relates to application of relatively short current pulses of constant subthreshold potential to medullated nerve (frog's sciatic at room temperature).

(1) The rise of electrotonus at the polarising pole is approximately or even exactly exponential.^{3, 14, 15} The duration of the development until it reaches $(1 - 1/e)$ of the maximum electrotonic potential is about 0.25 msec. This figure represents the time constant (k) if we assume the rise to be perfectly exponential. The final height is practically attained after 3 msec. The rate of rise decreases distinctly (and the height diminishes considerably) when the intermediate distance is lengthened. At the same time the curves obtain a slightly S-shaped form (Fig. 2).

The agreement between the function $\phi(\sqrt{\tau})$ (valid for intermediate distance $\xi = 0$; τ expressed in msec.) and the curve observed at the pole is not wholly satisfactory: the theoretical curve is initially steeper and subsequently flatter than the experimental curve. In Cremer's general solution ξ and τ are relative units of length and time defined by certain nerve constants. By suitable choice of their magnitudes the theoretical curves resemble the experimental records for different intermediate distances; particularly the S-shaped curvature is closely reproduced.³ The results are a qualitative confirmation of Hermann's conclusions.

(2) During the first few msec. there is no significant difference of magnitude between an- and catelectrotonic potential. Usually the ratio A : C is slightly smaller than unity, i.e., the increase of this proportion during the flow of the current is due to secondary alterations. The development of anelectrotonus is somewhat slower than that of

¹⁴ See Bogue, J. Y., and Rosenberg, H., *J. Physiol.*, 1934, **82**, 353.

¹⁵ Schmitz, W., and Schaefer, H., *Pflüger's Arch.*, 1933, **232**, 782; 1934, **233**, 229, 700; Schaefer, H., *ibid.*, 1936, **237**, 737.

catelectrotonus, and the disappearance of both lasts somewhat longer than the establishment.

(3) The electrotonus begins to rise simultaneously at all the extrapolar points with the make and to fall immediately with the break of the polarising current. Hence the speed of propagation related to the first start is extremely high in accordance with the theoretical postulate of "infinite" velocity. It lasts, however, a definite interval until a certain height of electrotonic potential is reached at a certain distance. If, for instance, the times required for the rise to a certain fraction of the maximum are plotted against the intermediate distances we find a fairly linear relation. This indicates that the electrotonic potential corresponding with this point of the curve travels along the nerve with a finite constant velocity. This velocity is about 9 m/sec. for the $1/2$ times, greater for the $1/e$ and smaller for the $(1 - 1/e)$ times of the rise to the maximum. (Any definite effect of electrotonus at an extrapolar

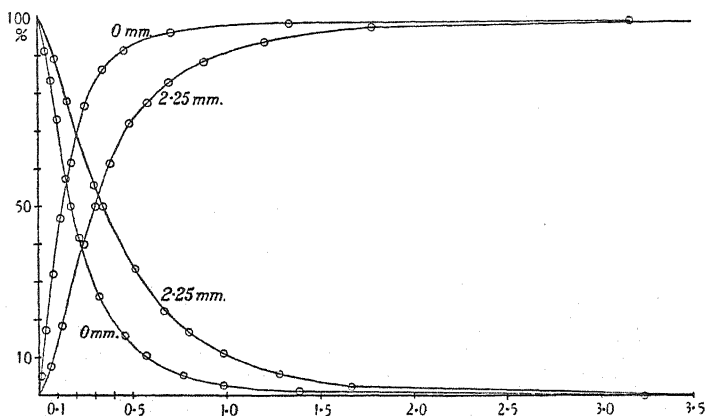


FIG. 2.—Catelectrotonic potentials at intermediate distances of 0 and 2.25 mm. resp. as percentages of the maximum values reached. Development upward, disappearance downward. Time in msec.

cross-section of the nerve obviously depends on the time factor of rise at the given distance and on the constant of the electrotonic potential gradient α . These factors reduce the "infinite" to a finite velocity.) The approximately linear relation follows, according to Cremer's information, from his theory which yields similar numerical values (for the theory of such pseudo-waves see Cremer^{16,17}).

In spite of the general agreement between experiment in nerve and core-conductor theory, a scheme with three fixed magnitudes is a sufficient description only of the very first changes during polarisation, as is known from measurements on real electrodes.¹⁷ In nerve, for instance, the final part of the rise of electrotonic potential generated by a short rectangular shock seems to indicate that the capacity gradually increases. The discrepancies which cannot be explained by the original theories are conspicuous in the electrotonic phenomena produced by sinusoidal currents.¹⁸ A new elaborate theory of the membrane core-

¹⁶ Cremer, M., *Z. Biol.*, 1900, **40**, 393.

¹⁷ See Lullies, H., *Pflüger's Arch.*, 1928, **221**, 296.

¹⁸ Harris, D. T., Rosenberg, H., and Sager, O., *J. Physiol.*, 1935, **86**, 4 P.

conductor¹⁹ interprets some of the difficulties, but in its present form it imposes restrictions which exclude the development of extrapolar electrotonus: an "infinite" length is attributed to the polar region along which the envelope (outer fluid conductor) is at electrode potential.

V. Catelectrotonus as a Condition of Membrane Instability (Excitation).

The influences of electrotonus on the reactivity of the nerve membrane are manifold (physiological electrotonus) and generally interpreted in terms of ion movement and permeability. The decisive question, however, remains: is electrotonus an artefact which—perhaps—reveals some functional properties or has it any significance in physiological action of nerve which essentially is conduction of impulses? Since it is possible to elicit a "propagated disturbance" by stimulation of any point of the nerve trunk it is a reasonable assumption that conduction actually is repetition of stimulation and excitation along the nerve. We suppose that this transmission from particle to particle is effected by a transitory potential change which accompanies action and evokes action.²⁰ Since any electrical variation in nerve is associated with physical electrotonus, we have to ascertain its part in stimulation (normally subthreshold catelectrotonus raises and anelectrotonus lowers the excitability).

We have some reason to believe that the potential which develops across the membrane, when an extrinsic electrical liminal stimulus is applied, and which is measured as catelectrotonic potential is the intrinsic stimulus; and that the threshold condition is the attainment of a certain electrotonic potential ("membrane charge") in the cathodic region. The physiological effect on the nerve membrane of this critical potential is the onset of excitation which in nerve is probably identical with the onset of a propagated wave of negativity. (In Lillie's model the critical potential corresponds with the break-down condition of the oxide film.) This hypothesis of stimulation is based on the following facts.

(1) At threshold stimulation with direct current, underneath the cathode the action potential appears when the electrotonic rise has nearly reached its maximum.^{14, 15} The time interval between make and electrical response at the excited point equals the required minimum duration of a constant current pulse in threshold stimulation.²¹ Hence under these conditions excitation occurs when the electrotonic potential at the cathode is almost fully developed. The same conclusion applies to threshold stimulation with relatively slow condenser discharges.

(2) If a finite subliminal catelectrotonic potential is taken as an index and the "thresholds" are determined for condenser discharges of different duration and potential, the voltage-capacity relation obtained fits exactly the experimental and theoretical²² curve for liminal excitation.²³ If the distance of the polarising electrodes is diminished, e.g., from 20 to 2 mm., the time constant of the curve is shortened to a similar extent in both catelectrotonus and excitation.²⁴ This result is in accordance with the core-conductor conception.

¹⁹ Labes, R., *Z. Biol.*, 1932, 93, 42, 191.

²⁰ Hermann, L., *Handb.*, 1879, 2, 186.

²¹ Blair, E. A., and Erlanger, J., *Amer. J. Physiol.*, 1936, 114, 317.

²² Hill, A. V., *Proc. Roy. Soc., B*, 1936, 119, 395, 440.

²³ Harris, D. T. and Rosenberg, H., *J. Physiol.*, 1935, 84, 11 P.

²⁴ Rosenberg, unpublished.

(3) If the "threshold" intensities for this catelectrotonic index are measured at different frequencies of sinusoidal current, the $I^2 - n^2$ relation calculated from the data observed is linear between 300 and 1200 hz. as theoretically predicted and experimentally confirmed²⁵ for nerve stimulation. The time constant derived in this way is the same as in polarisation by condenser discharges.²⁴

In the three cases the time constant k of electrotonus at the cathode is about $1/2 - 2/3$ of that obtained in excitation. As a tentative solution of this discrepancy it is suggested that k for electrotonus at the cathode concerns the alteration of a cross-section immediately underneath the pole whereas the initiating process has to affect a region of finite length in order to provoke a propagated disturbance. Since, as shown, the electrotonic time constant increases approximately in proportion with the intermediate length, at a certain distance k for electrotonus equals k for excitation.

These results support the assumption that the cathodic *potential* which is manifested as electrotonus is the intrinsic stimulus for the nerve membrane in physiological activity.

²⁵ Hill, A. V., Katz, B., and Solandt, D. Y., *Proc. Roy. Soc., B.*, 1936, **121**, 74.

THE PHYSICAL AND CHEMICAL PROPERTIES OF NERVE FIBRES AND THE NATURE OF SYNAPTIC CONTACTS.

BY J. Z. YOUNG, M.A.

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Recent studies with optical and chemical methods make it possible to construct a picture of the chemical morphology of the nerve fibre which, with slight modifications, will apply to all known types of nerve.

Each portion of the fibre may be considered as consisting of concentric layers, differing in composition, the outermost layer being the tissue lymph, a complex solution of inorganic ions, metabolites and plasma proteins. Embedded in this medium is the nerve fibre proper, whose outer region consists of one or more layers of a scleroprotein, probably mainly collagen. This layer of connective tissue merges with the loose network which permeates the nerve (endoneurium), and is in turn continuous with the perineurium surrounding the whole bundle.

The collagenous sheath of each fibre is usually very thin in vertebrates (Henle's sheath), but in Crustacea and Molluscs it may consist of several concentric layers. The protein molecules are grouped into fibrils, each anisotropic and having some regular internal molecular organisation. These fibrils in turn are arranged around and along the nerve fibre to form enclosing sheets. Interspersed among the collagenous fibrils are fibroblast cells, but the collagen itself is an intercellular substance as strictly as are the proteins of the lymph. Moreover the lymph appears to penetrate between the separate layers of collagen,¹ so that we may regard this outer region of the fibre as consisting of alternate layers of collagenous and lymph proteins, with inorganic ions distributed through both phases.

¹ Young, J. Z., *Symp. Quant. Biol.*, 1936, **4**, 1; *Proc. Roy. Soc., B*, 1936, **121**, 319.

The reason for drawing attention to this outer sheath is its astonishing thickness in some cases. In the large fibres in the leg nerves of *Maia* it is several times thicker than the axon itself, and in the case of the single fibre which innervates the electric organ of the catfish *Malapterurus* the axon and its myelin sheath measure together 10μ whereas the outer wrappings give the whole fibre a diameter of nearly one millimetre.² It would be unwise to neglect these outer sheaths as being of supporting function only. Their great thickness in the nerve to the electric organ, whose axon has to be protected from large voltages, suggests that they may have an insulating function; in which case they are presumably not freely permeated by inorganic ions. It is perhaps also significant that these outer layers are thinner around the well-medullated fibres of vertebrates than around those of invertebrates which as will be shown have only a very thin myelin-like layer.

Myelin Layers.

Inside the collagenous layers lies a region whose most striking component consists of fatty substances, mainly cerebroside and cephalin, which are anisotropic, behaving as optically uniaxial micelles whose axes are oriented radially with respect to the whole fibre. In some cases (vertebrates, earthworms, prawns) this layer is readily revealed by staining with osmium tetroxide, such fibres being known as medullated fibres. In other cases, such as the nerves of Crabs or Cephalopod Molluscs this layer cannot be seen with ordinary histological methods and its presence can only be deduced from study of the birefringence of the nerves.³ Such nerves are usually said to be non-medullated, but may conveniently be described as having a myelin-like sheath.

In vertebrates the orientation of the lipoids gives to this layer the negative birefringence with respect to the length of the fibre which is so characteristic of the myelin sheath. The so-called non-medullated nerves do not show this negative birefringence in the fresh state, the sheaths being positively birefringent on account of the orientation in the protein which they contain. However it has long been known that a certain part of the sheath will become negatively birefringent when treated with fluids of appropriate refractive index, such as dilute glycerine, this reversal being called the metatropic reaction.⁴ Schmitt and his collaborators have recently shown that the reversal is not due to orientation of the substance produced by dehydration as Göthlin supposed, but can be interpreted on the assumption that the layer in question contains protein molecules having a positive form birefringence which disappears when the nerve is soaked in a medium of appropriate refractive index, leaving a negative birefringence due to radially oriented fatty micelles.

The myelin layer of vertebrate nerves is known to contain protein as well as fatty material and it is suggested that the protein and lipid are arranged in alternate layers, the fat preponderating in the medullated fibres, the protein in the "non-medullated." The distinction between these two types thus largely disappears.^{3b}

In vertebrates the birefringence of the sheath, and hence the proportion of lipid which it contains decreases with the diameter of the axon, the sheaths of fibres of about 2μ being positively birefringent ("non-medullated"), and Schmitt suggests^{3b} that the relative amount of fat in the sheath may be an important factor in determining conduction velocity.

The myelin and myelin-like sheaths are produced by special layers of cells, in vertebrates the ectodermal Schwann cells and oligodendroglia, lying be-

² Fritsch, G., *Die elektrischen Fische*, Leipzig, 1887.

³ (a) Schmitt, F. O., Bear, R. S., and Young, J. Z., *Biol. Bull.*, 1936, **71**, 402.

(b) Schmitt, F. O., *Symp. Quant. Biol.*, 1936, **4**, 7.

⁴ Göthlin, E. F., *K. svenska. Vetenskad. Handl.*, 1913, **51**, 1.

tween the myelin and collagenous layers, and in Cephalopods and Crustacea by a sheath lying between the myelin-like layer and the axon itself (Fig. 1). The significance of this inner position of the Schwann-like sheath of these invertebrates is still quite obscure.

In the case of vertebrate nerves the myelin sheath is not continuous over the whole surface of the axon, but is interrupted at intervals by the nodes of Ranvier, and it is possible that the incisures of Lantermann represent further interruptions of its continuity. In Cephalopods the myelin-like layer is continuous over the whole surface of the fibre, and this is probably true also of Crustacea, though partial constrictions have been described by Nageotte⁵ in prawns.

Both in vertebrates and invertebrates there may perhaps be a layer of lymph ("periaxial space") between the myelin and the surface of the axon, but if present it must be excessively thin, and micro-dissection studies in vertebrates have shown that the myelin adheres to the surface of the axon.⁶ Even the inner Schwann-like layer of Molluscs and Crustacea is

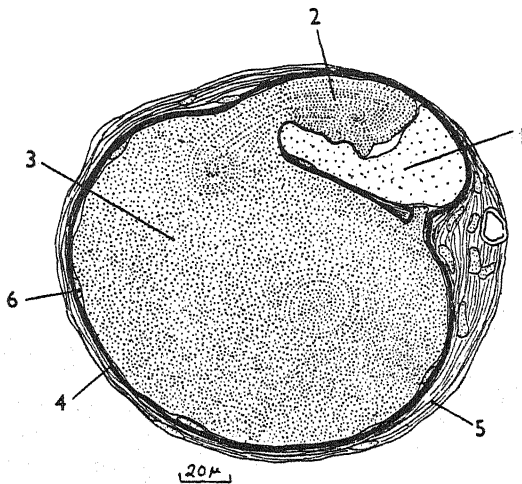


FIG. 1.—Transverse section of synapse on giant nerve fibre in the stellate ganglion of *Loligo*. The more lightly-stained fibre 1 comes from the C.N.S. and makes contact with collaterals, 2, of the more darkly-staining fibre 3, which arises from cells in the ganglion and runs to the muscles. The myelin-like sheath, 4, is shown in black, but cannot be distinguished, in the actual preparation, from the outer sheaths, 5. Several nuclei of the inner protoplasmic sheath are shown, 6.

only distinguishable under favourable conditions, and the axon is closely pressed against it. However such "spaces" between the surface of the axon and the myelin become larger under pathological conditions⁷ and it is possible, though unlikely, that there is always a watery layer in this region.

Composition of the Axon.

It is still debated whether the axon (axis cylinder) which forms the central portion of each nerve fibre shows longitudinal striations (neurofibrils) during life. Weiss and Wang⁸ have shown that such fibrils can be observed in living chick neuroblasts cultured *in vitro*, but this does not necessarily indicate that they occur as such in the body. Speidel⁷ was unable to observe them in living intact axons of the tadpole's tail, and both he and Young¹ found that they became much more definite when the axon was mishandled in any way. It is certain that fibrils can very readily be made to appear in the axon, which strongly suggests that at least part of the substance of the axoplasm consists of molecules or micelles orientated with their long axes parallel to the length of the fibre. This is strongly confirmed

⁵ Nageotte, J., *L'organisation de la matière dans ses rapports avec la vie*, Paris, 1922.

⁶ de Renvi, G. S., *J. Comp. Neurol.*, 1929, 48, 293.

⁷ Speidel, C. C., *Sym. Quant. Biol.*, 1936, 4, 13.

⁸ Weiss, P., and Wang, H., *Anat. Rec.*, 1936, 67, 105.

by the fact that the axoplasm is anisotropic, being uniaxially birefringent, positive with respect to the length of the fibre. The degree of this birefringence has recently been calculated ^{2a, 9} in the case of the giant axons of the squid (*Loligo*), and found to be of the order of 1.5×10^{-4} , made up partly of form and partly of intrinsic birefringence.

There is still very little information about the chemical properties of the contents of the axon. Using the pure axoplasm which can be pressed out from the very large nerve fibres of *Loligo* we ^{2a, 9} have made a beginning with the study of the proteins present. The great part of the protein is readily soluble in alkali (p_H 11 to 14) and a histone or protamine-like fraction separates from the solution on standing. The protein is readily precipitated in acid. With care a fraction can be separated off which resembles nucleic acid in being soluble in dilute acid (p_H 5), but precipitated by strong acid or by acidified alcohol. The presence of phosphorus, purine bases and desoxy sugars is suggested by tests applied to this nucleic acid-like fraction, but the amounts of material available have been too small for the tests to be conclusive. However extracts from other nervous tissues (Mammalian spinal cord, lobster nerves) contain a protein which is very closely similar to that present in the axon itself in *Loligo*, and from the protein of these extracts phosphorus and the purines can readily be identified. Since the studies on the Squid axons demonstrate that this protein occurs within the axon itself rather than in the interstitial tissues we are justified in concluding that nerve cells in general contain as one of their characteristic components a nucleic acid-containing complex which we propose to call neuronin.

There are, of course, numerous other substances dispersed in the axoplasm. Some lipid is present since myelin forms can be obtained from the pure axoplasm of *Loligo*. In addition there must be a host of metabolites and enzyme systems, not to mention the inorganic ions, the details of whose concentrations are still imperfectly unknown.

The axoplasm is therefore a colloidal system of the very greatest complexity, about which we know as yet extremely little, not nearly enough to say anything with confidence about the type of membrane which might be formed at an axoplasm-aqueous or axoplasm-lipoid interphase. Still less can we from the physics and chemistry of the axon form any clear picture of how the action and injury potentials are produced. Our best efforts are but analogies, which must not be accepted as accounts of the actual conditions.

Some light may perhaps be thrown on these questions by considering the differences in constitution along the length of each neuron, data about which are, however, unfortunately almost exclusively histological rather than physical or chemical. It is not generally realised that axons vary in composition along their length. Thus in the Squid (*Loligo*) the giant fibres which bring about contractions of the mantle of the animal are arranged on each side in chains of three nervous units, and in each unit the dendrites and proximal part of the axon are more deeply basophil than the distal part. As a result each synapse consists of a zone of contact between lightly- and darkly-stained substances (Fig. 1).

Similarly in earthworms the staining differences observed by Stough ¹⁰ may be interpreted as showing the existence of a gradation in the axoplasm so that the region which receives the impulse is more basophil than that which passes it on. There are insufficient data at present to allow us to decide whether this difference is a universal one, but there are other facts which suggest that the metabolism of axons is not uniform along their whole length.

The gradation in stainability along the axon may perhaps be connected with the occurrence in the cell body of large masses of basophil substance,

⁹ Bear, Schmitt, and Young, *Proc. Roy. Soc. (in the press)*.

¹⁰ Stough, H. B., *Jour. Comp. Neurol.*, 1926, 40, 409.

the Nissl substance. Although this is sometimes sharply marked off from the axon by a clear "axon hillock" yet in many other cases the minute granules of Nissl substance grade imperceptibly into the flecks of basophil material which in fixed preparations give the axon its fibrillar appearance. It seems not at all improbable that we are dealing in both cases with the same protein, present in much greater amounts in the cell body than in the axon.

It is perhaps premature to speculate further on this gradation along the course of the axon, but it is by no means impossible that it is very intimately connected with the mechanism of conduction, especially if the production of the electromotive forces in nerve depends on a diffusion potential involving the escape of a large colloidal anion and a faster moving cation, perhaps K^+ .¹¹ It is known that a portion of the protein present in crustacean nerve can escape by diffusion.¹² Making a further guess we might suppose the Nissl substance to be the source of supply of this diffusible material which would explain the disappearance of the Nissl substance during fatigue or after section of the axon.

These are highly speculative assumptions, which may be open to various objections as they stand. The hypothesis can, however, be tested experimentally in several ways and the two facts upon which it is based, namely that staining differences do occur along the length of the nerve and that the axon is trophically dependent on the cell body must in any case be taken into account. Incidentally it may be pointed out that if the normal functioning of peripheral nerve involves the leaking of a large ion, then the distinction between conduction in peripheral nerve and humoral synaptic excitation becomes less marked than it at present appears. However the information available is far too scanty to allow any proper development of this point of view.

The picture which has been presented of each nerve fibre as a cylinder composed of various layers is necessarily as yet a very crude one. In particular we know almost nothing of the boundary conditions between the different phases. Indeed it is not clear exactly in what sense, with the optical, physical and chemical techniques which have hitherto been applied to nerve, we can properly speak with any knowledge of "membranes" at all. We know only that certain immiscible phases are present and that somewhere in the system the conditions are such that a variable electrical potential is set up between the inside and the outside of the whole unit.

In attempting to give an account of the factors which control this potential it is worth considering whether, instead of laying emphasis on a particular membrane, we should be wise to study the powers of diffusion away from the centre of the unit, and the effect on these diffusion rates of the various sheath elements. Although the surface of the axon itself is obviously a region of especial importance, yet it is improbable that any consideration of this surface alone, in terms of analogies with artificial membranes, will give us a satisfactory picture of the propagation of the nerve impulse.

Synaptic Contacts.

Some light is thrown on the part played by the various phases by study of the condition at synapses. In Cephalopods the synapses of the giant nerve fibres can be studied with cytological methods as well as with the cruder impregnation methods generally used by neurologists. It is found that at the synapse the surfaces of the axoplasm of each of the two fibres concerned are in contact. The myelin-like sheath does not extend between the two axons at this point (Fig. 1). The work of Bartelmez and Hoerr¹³

¹¹ See Amberson, W. R., *Symp. Quant. Biol.*, 1936, 4, 53, for discussion of such a view.

¹² See Schmitt's remarks in discussion of the paper of Amberson.¹¹

¹³ Bartelmez, G. W., and Hoerr, N. L., *J. Comp. Neurol.*, 1933, 57, 401.

suggests that a similar close contact of the surfaces of the axons occurs in the Mauthner cell synapses in fishes, which are the only others which have yet been studied in sufficient detail to allow this point to be determined.

In the Cephalopods it is very striking to see how mere contact between two fibres enclosed in their sheaths is evidently not sufficient for synaptic transmission, which can only be effected by means of collaterals from the one extending *inside the myelin-like sheath of the other*. This perhaps indicates that these sheaths serve to prevent the spread of electric currents away from one fibre to other fibres, and perhaps they actually canalise such effects along the length of the fibre.

These histological and physico-chemical studies, therefore, though they do not definitely indicate the nature or site of origin of the electromotive forces developed by the nerve, yet give certain important limiting data. It seems probable that diffusion away from the axoplasm is responsible, in some way, for the injury and action potentials, the fatty and perhaps also the outer sheaths profoundly modifying the potential by the conditions which they impose close to the surface of the axon. In particular the existence of a thin layer of radially oriented lipid molecules, even around nerves which by histological methods appear to be "non-medullated," reinforces the suspicion that such an arrangement plays some particularly significant part in the mechanism of nervous conduction.

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THE BIOELECTRICAL PROPERTIES OF FROG SKIN.

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Physiological Introduction.

It has been known since the time of du Bois Reymond¹ that there is a difference of electrical potential across frog skin which can therefore be used in investigations of bioelectricity. The advantages of using this tissue are that it can be mounted as a flat membrane, that it can be cut into pieces so as to allow living controls off the same frog, and that it is easily and rapidly prepared. Though less interesting, perhaps, from a physiological point of view than nerve or muscle it plays a rôle in regulating water,² ionic,³ and respiratory⁴ exchange between the frog and its environment, in this respect its behaviour being somewhat analogous to that of the cell membrane of a unicellular organism. The disadvantages of using frog skin are first that it is a multicellular tissue, which increases the possibilities of complications arising from topochemical factors, and secondly that it is variable, standard deviations per observation of some 25 per cent. being observed⁵ with the electrical

¹ du Bois Reymond, *Unters. über Thier. Elektr.*, 1857 (ii) 9.

² Durig, *Arch. ges. Physiol.*, 1901, 85, 401; Overton, *Verhand Physiol. Med. Ges. Würz.*, 1904, 26, 277; Adolph, *Am. J. Physiol.*, 1925, 73, 85; *J. Exp. Zool.*, 1925, 43, 105; *ibid.*, 1927, 47, 1; Brunacci, *Z. Physiol.*, 1912, 25, 1167.

³ Krogh, *Skand. Arch. Physiol. (in the press)*; Overton²; Adolph.²

⁴ Krogh, *Skand. Arch. Physiol.*, 1904, 15, 328; Dolik and Postma, *Z. Physiol.*, 1927, 5, 417.

⁵ Francis and Gatty, *J. Exp. Biol. (in the press)*.

potential, the electrical resistance, and the Q_{O_2} (mm^3O_2 at N.T.P. consumed gm^{-1} dry weight per minute). All published work on frog skin should be accompanied by adequate statistical control; lack of this reduces the value of much of the published work on skin potentials. Most of the work has been done on *Rana temporaria* in Europe, on *R. pipiens* in the United States, and on *R. nigromaculata* in Japan. Other species used were *R. esculenta* and *R. catesbiana*. Differences between the species do not seem very marked except that skins of *R. catesbiana* gave higher potentials.⁶

The Inadequacy of the Formulæ for Liquid-Liquid Junction Potentials in Bioelectric Systems.

Many workers⁷ have attempted to relate bioelectric potentials with ionic mobilities by the use of the integrated formulæ for diffusion potentials.⁸ This work is liable to be unsound for three reasons:—

(1) Because of the possibility of the ions having to penetrate a non-aqueous phase.

(2) Because of the thickness of many biological membranes.

(3) Because of the possibility of local action currents⁹ which leads to the further possibility of modifications of potential due to ion adsorption of the type called specific adsorption in electrocapillary work.¹⁰ Owing to the thickness of the membrane the different surfaces giving rise to local action currents have to be considered in three dimensions instead of two as for the simpler case of corroding metals.

(1) The unintegrated formula given by Guggenheim¹¹ for liquid-liquid junction potentials is readily extended in theory to systems containing more than one solvent but allowance has to be made for the free energy of transfer of ions from one solvent through mixed solvents to another solvent; this affects the chemical potential of ions in their standard states. Inadequate knowledge of free energies of solvation precludes the use of accurate formulæ in all but the simplest chemical systems.

(2) The thickness of biological "tissue-membranes" introduces the possibility of the tissue acting as a storage vessel and increases the possibilities of variation of ionic mobilities throughout the membrane. The effect of absorption of solute and solvent by a membrane on the direction of osmosis of systems not in equilibrium has been discussed by Schreinemakers¹² and Schreinemakers and Werre.¹³ All these effects have only to be considered in terms of diffusion of ions to show that corresponding diffusion potentials will arise. These effects may lead to one or more diffusion potentials being maintained through a single tissue. Steinbach's¹⁴ results in a few cases indicate the existence of opposing potentials in frog

⁶ Klopp, *J. Gen. Physiol.*, 1924, **7**, 39.

⁷ Osterhout and co-workers, *J. Gen. Physiol.*, for the best work on these lines.

⁸ Planck, *Wied. Ann.*, 1890, **40**, 561; Henderson, *Z. physik. Chem.*, 1907, **59**, 118; 1908, **63**, 325.

⁹ Evans, *Metallic Corrosion, Passivity and Resistance*, Arnold, 1937.

¹⁰ Stern, *Z. Elektrochem.*, 1924, **30**, 508; Craxford, Gatty and co-workers, *Phil. Mag.*, 1933, **14**, 1849; 1934, **17**, 54; 1935, **19**, 965; 1936, **22**, 359.

¹¹ Guggenheim, *Modern Thermodynamics*, Methuen, 1933; *J. Physic. Chem.*, 1930, **34**, 1758. Also Unmark and Guggenheim, *Kgl. Dansh Vid. Selsk.*, 1930, **10**, Nos. 8 and 14.

¹² Schreinemakers, *Prok. K. Akad. Wetensch. Amst.*, 1929, **32**, 837, 1024, 1305; 1930, **33**, 119; 1931, **34**, 78, 344, 524, 823, 1282; *Rec. Trav. Chim.*, 1931, **50**, 222, 883, 1932; **51**, 218.

¹³ Schreinemakers and Werre, *Rec. Trav. Chim.*, 1932, **51**, 51; *Prok. K. Akad. Wetensch. Amst.*, 1932, **35**, 42, 162.

¹⁴ Steinbach, *J. Cell. and Comp. Physiol.*, 1933, **5**, 1.

skin (only in the case of small potentials) though he states they prove the contrary conclusion. His skin electrode made contact, however, with the inner and outer sides and also a cut edge of the skin and such a potential is hard to interpret. Potentials arising from diffusion across a portion only of the membrane will be referred to below as "absorption potentials"; they may not be important in the case of unicellular membranes.

(3) Local action currents must exist on frog skin. Different halves of the belly skin of one frog are often observed to have potentials that differ by over 50 per cent.⁵ so that the whole skin if mounted would show local action currents. In addition there is evidence that there occurs across frog skin a certain amount of internal short circuiting which is a special case of local action currents. Motokawa¹⁵ finds that stretching the skin by supplying excess of hydrostatic pressure to either side reduces the potential, irrespective of its sign, towards zero. The magnitude of the effect increases with increasing pressure. There is also a marked positive correlation¹⁵ for variations in composition of solution between the magnitudes of the potential and its depression by a given pressure.

The hypothesis that the "pressure effect" is primarily due to internal short circuiting is supported by observations¹⁵ that rate of diffusion of sodium chloride outwards through the skin is increased by stretching, while Rubin¹⁶ found that K^+ is liberated by an interrupted air jet playing on frog skin. Direct measurements of electrical resistance¹⁷ show that the stretching produced by altering the sign of the curvature of frog skin, which normally is convex towards its outer side, lowers the resistance and also the potential. If the latter is very small owing to the effects of p_H 6, $M/500$ NaCN, permanganate, or potassium substituted for sodium the "positional effect" on the resistance persists but that on the potentials vanishes, as would be predicted by the short circuiting theory. The former two reagents raise the resistance for some hours and the latter two reduce it.¹⁷ Lund¹⁸ even suggests that different polarities at opposite ends of single cells produce the skin potential which results from many cellular units connected both in series and in parallel. His view implies both that local action currents exist between points on the surface of the same cell and also (*cf.* Danielli)¹⁹ indirectly that elastic as well as surface tension forces are needed to maintain the cell membrane.

The importance of demonstrating the existence of local action currents is that the observed potential is to be related not to the formulæ for liquid-liquid junction potentials but to the more general principles involved in determining the electrode potentials of corroding metals.²⁰ The conditions that are important are (1) zero nett flow of charge across the membrane when balanced in a potentiometer, (2) the nature of the different possible surfaces in the system, (3) their relative magnitudes and positions, (4) the rates of the different reactions proceeding at these surfaces and their relationship to potential differences across them. The membrane in fact becomes a mosaic membrane.²¹

Strong adsorption of an ion at a surface introduces a considerable area of a new surface field,²² and this may affect reaction velocities over the membrane. Thus specific adsorption may affect potentials in systems where local action currents are proceeding but cannot shift the potential of an ideal thermodynamical electrode. These potentials will be referred to below as "adsorption potentials."

¹⁵ Motokawa, *Jap. J. Med. Sci. Biophys.*, 1933, **3**, 117 and 145.

¹⁶ Rubin, *J. Gen. Physiol.*, 1936, **19**, 135.

¹⁷ Gatty (*unpublished*).

¹⁸ Lund, *J. Exp. Zool.*, 1928, **51**, 265.

¹⁹ Danielli, *J. Cell and Comp. Physiol.*, 1934, **5**, 495; 1935, **7**, 393.

²⁰ Gatty and Spooner, *Electrode Potentials of Corroding Metals*, Oxford (*in the press*).

²¹ Söllner, *Z. Elektrochem.*, 1930, **36**, 36, 234; *Biochem. Z.*, 1932, **244**, 370, Grollman and Söllner, *Trans. Am. Electrochem. Soc.*, 1932, **61**, 81, 89; *Z. Elektrode*, 1932, **38**, 274.

²² Langmuir, *J. Chem. Physics*, 1932, **1**, 1.

The effect of pressure variations across frog skin have been used to make a microphone by Gatty and Rawdon-Smith²³ who suggest that a similar phenomenon with Reissners membrane would account for the Wever and Bray effect.²⁴

Dead Skins.

The behaviour of dead frog skin suggests that absorption and adsorption potentials are not important; the behaviour of living frog skin is extremely difficult to interpret on any theory not involving one or other of these potentials. Dead frog skin behaves like an ampholytic membrane which is cation permeable in solutions on the alkaline side of its isoelectric point, anion permeable in solutions on the acid side of its isoelectric point, and relatively impermeable to highly charged ions of either sign. This is brought out by Amberson and Klein²⁵ whose work on the change, with changing p_H of the sign of potentials with dilute solutions on the outside of the skin has been confirmed by Motokawa.²⁶ This last worker^{26, 27} showed that potentials arising from concentration gradients across skins killed in a variety of ways could be interpreted in terms of diffusion potentials and an ampholytic colloidal membrane. It behaves rather like egg-white in the work of Mond,²⁸ Deutsch,²⁹ and Matsuo.³⁰ Amberson and Klein²⁵ give further confirmation by their measurements of electrosmosis by the method of Mudd.³¹ The "stirring effect" of Motokawa²⁷ is probably due to resultant modifications of diffusion rates since König³² shows that electrokinetic changes of potential are only to be expected at rates of motion comparable to ions when showing the Wien effect.³³

Ionic Composition of Solutions and Potentials of Living Frog Skin.

The effect of varying ionic compositions and concentrations on the potential of frog skin has been investigated by Hashida,³⁴ Uhlenbruck,³⁵ Steinbach,³⁶ and by Motokawa.³⁶ Confirmation of much of their work has been obtained³⁷ using adequate statistical controls and paying greater attention to the time factor. The resistance and polarisation of frog skin have been investigated by alternating currents,³⁸ by direct currents,³⁹ and at constant currents by Pumphrey,⁴⁰ and this work has been extended.⁴¹

²³ Gatty and Rawdon Smith, *Nature (in the press)*.

²⁴ Wever and Bray, *J. Exp. Psych.*, 1930, **13**, 373.

²⁵ Amberson and Klein, *J. Gen. Physiol.*, 1928, **11**, 823.

²⁶ Motokawa, *Jap. J. Med. Sci. Biophysics*, 1933, **3**, 69.

²⁷ Motokawa, *Jap. J. Med. Sci. Biophysics*, 1933, **3**, 95. Cf. also Hashida, *J. Bioch.*, 1922, **1**, 289.

²⁸ Mond, *Pflug. Arch.*, 1924, **203**, 247.

²⁹ Deutsch, *Pflug. Arch.*, 1925, **209**, 675. Cf. also Fugita, *Bioch. Z.*, 1925, **162**, 245.

³⁰ Matsuo, *Pflug. Arch.*, 1923, **200**, 132.

³¹ Mudd, *J. Gen. Physiol.*, 1926, **9**, 361.

³² König, *J. Physic. Chem.*, 1935, **39**, 455.

³³ Wien, *Ann. Physik. (IV.)*, 1924, **73**, 161; 1925, **77**, 560; 1927, **83**, 327; 1928, **85**, 795; (V.), 1929, **1**, 400; *Physik. Z.*, 1927, **28**, 384; Malsch and Wien, *Ann. Physik. (IV.)*, 1927, **83**, 305, and *Physik. Z.*, 1927, **28**, 834.

³⁴ Hashida, *J. Biochem.*, 1922, **1**, 21.

³⁵ Uhlenbruck, *Z. Biol.*, 1924, **82**, 225.

³⁶ Motokawa, *Jap. J. Med. Sci. Biophysics*, 1935, **3**, 177.

³⁷ Dean (unpublished).

³⁸ Lullies, *Pflug. Archiv.*, 1929, **221**, 296.

³⁹ Hashida, *Jap. J. Med. Sci. Biophysics*, 1932, **2**, 290.

⁴⁰ Pumphrey, *J. Exp. Biol.*, 1934, **11**, 423 and 429.

⁴¹ Dean and Gatty (unpublished).

Replacing ³⁷ the Na⁺ in Ringer solution on both sides of the skin by Rb⁺, Cs⁺, NH₄⁺, Ca⁺⁺, or Mg⁺⁺ causes a reversible drop of potential to some + 3 millivolts (positive potentials are defined as ones where the electrode in the solution in contact with the morphologically inner side of the skin is the more positive) from the Ringer-Ringer potential at p_H 8 of some + 40 millivolts. Replacing by potassium reduces the potential to zero. Higher potentials but still below the Ringer-Ringer potential are observed if the substitution is on either side only of the skin. Replacing ³⁷ Na⁺ by Li⁺ causes little change in potential during the first hour when measurements of potential are made at 20-minute intervals (Takanake,⁴² however, reports that lithium salt solutions isotonic with Ringer when put on the outside of the skin lead to quasi-periodic fluctuations of potential). The "sodium effect" just described was also recorded in the case of isotonic solutions of salts of the above-mentioned cations by several workers.^{34, 35, 36} Adolph² reports that sodium solutions hypertonic to Ringer unlike similar solutions of K⁺, NH₄⁺ or Ca⁺⁺ alter frog skin permeability so as to permit increased entry of water into living frogs.

Using Ringer at p_H 8 on the inside of the skin and any dilute solution such as tapwater, pond water, or Ringer less varying amounts of sodium chloride, lower potentials are observed than for external Ringer solution; ³⁷ in sodium free dilute solutions potentials of - 30 to - 40 millivolts are obtained. These results have also been observed by several workers.^{14, 25, 34, 35, 36} On flowing solutions richer in sodium back on to the outside of the skin the potential rises rapidly from negative to high positive values ³⁷ from which it falls back more slowly to the new steady positive potential. A rather similar effect is observed with Li⁺. With K⁺, NH₄⁺, Ca⁺⁺, Hg⁺⁺, Mn⁺⁺ and Ca⁺⁺⁺ the potential rises to a value close to zero as it does with M/10 HCl but in all these cases the rise is much slower.

The complete substitution of chloride by NO₃⁻, SO₄⁻, CH₃.COO⁻, (CH₃COO)₂⁻, citrate⁼, IO₃⁻, (COO)₂⁻, HPO₄⁻, Br⁻, F⁻, or CNS⁻ in the Ringer in contact with the outside of the skin gives a quick rise in potential which is not observed in Ringer in which the Na⁺ has been replaced by K⁺ (only NO₃⁻ tried).³⁷ Some of these observations conflict with some of Hashida's,³⁴ but he tried the anions after dilute solutions and not after Ringer and had no adequate statistical control. Some of the above results have been recorded previously by Uhlenbruck.³⁵ Substitution of the chloride by bicarbonate on the outside, however, lowers the potential ³⁷ and raises the electrical resistance subsequent use of bicarbonate with Ringer on the inside of the skin tending to restore the potential.

The potential is not much affected ³⁷ by p_H 's between 7.6 and 8.6, but outside this range it falls irrespective of whether the solution is acid or alkaline or whether it is applied to either or both sides of the skin. Absence from both sides of the skin of K⁺ is slightly toxic to skin potential but for an hour or so the absence of Ca⁺⁺, HCO₃⁻, and HPO₄⁻ is not toxic nor that of HCO₃⁻ and H₂PO₄⁻ together if the Ringer is suitably buffered by glycine. Absence both of Ca⁺⁺ and HCO₃⁻ is toxic even in the presence of buffers.³⁷

Concentration gradients of M/20 to zero across the skin in either direction of lactate, acetate, propionate and succinate show no effect on the potential.⁵ Pumphrey⁴⁰ showed that the electrical resistance of the skin is reduced in potassium rich Ringer solutions and this result has been confirmed.¹⁷

The sodium effect shows that a 60:1 concentration ratio of (1/pM²⁺ - Na⁺) across the skin lowers the potential irrespective of the direction of the concentration gradient where M²⁺ is K⁺, Rb⁺, Cs⁺, NH₄⁺, Ca⁺⁺ or Mg⁺⁺. It is inferred that the contribution to the total skin

⁴² Takanake, *Jap. J. Med. Sci. Biophysics*, 1936, 4, 143.

potential of the diffusion potentials of $(1/pM^{p+} - Na^+)$ is small. The big effect on the potential, being irrespective of the direction of the concentration gradient, is probably due, therefore, to the combined effects of adsorption and absorption potentials. It seems likely that different sides of the skin behave differently as regards the differential adsorptions and absorptions of $(1/pM^{p+} - Na^+)$. Moreover, the magnitude of the adsorption and absorption potentials is great enough to reverse any potential, should there be one, arising from the formation of respiratory ions in the skin; thus there is the change of sign of potential by the dilution effect; moreover, the respiratory poison CN^- reduces positive potentials towards zero if Ringer is on both sides of the skin; if, however, the outside is in contact with $M/500$ KCl the negative potential becomes more negative when the inner Ringer is replaced³⁷ by Ringer + $M/500$ NaCN. The outside of the skin ad- or absorbs sodium ion quicker than chlorine ion or than any other cation tried so far with lithium as the next best; of the anions bicarbonate is ad- or absorbed the most and chloride is next best. This is inferred from rates of recovery from the "dilute-solution" effect and from chloride effect results. The depth over which the sodium effect occurs is probably small, thus the quick entry of sodium compared to potassium shows that it involves more than large aqueous pores, where the two ions should have a comparable mobility; the fact that potassium rich Ringer has a lower resistance suggests that for most of the skin K^+ has a higher mobility than Na^+ . With dilute solutions on the outside the potential should be positive instead of negative if the potential is due to diffusion of Cl^- . Similar arguments dispose of p_H gradients as the source of the potential. These data are insufficient to decide between adsorption and absorption potentials, however. Hashida³⁴ pointed out the importance of adsorption potentials and Motokawa³⁸ has obtained a semi-quantitative explanation of the effect of osmotic pressure and varying salt concentrations on skin potentials in terms of ionic adsorption.

Recent Work on the Connection between Potential and Oxygen Uptake.

The connection between oxygen uptake and potential was investigated by Mansfield⁴³ and established by Lund and co-workers.⁴⁴ The latter school spoil some of their discussions by failing to realise that redox reactions, qua redox reactions, only give rise to differences of electrical potential in the presence of electron donors and acceptors like metallic electrodes. Francis and Pumphrey,⁴⁵ Francis,⁴⁶ Boell and Taylor⁴⁷ and Taylor,⁴⁸ and Ponder and Macleod⁵⁰ have all confirmed and extended the results of Lund. Their results are referred to in further extensions of the work by Francis and Gatty.⁵ It appears that in addition to internal supplies of carbohydrate external supplies of *dl*-lactate, pyruvate, acetate, propionate, *n*-butyrate, isobutyrate, and possibly crotonate by their oxidation can supply precursors of electrical potential. This is not so for external supplies of formate, glycollate, succinate, acrylate, malonate, *dl*- β -hydroxybutyrate and acetoacetate.⁵

⁴³ Mansfield, *Pflug. Archiv.*, 1910, **131**, 457.

⁴⁴ Lund, *J. Exp. Zool.*, 1925, **41**, 155; 1926, **44**, 383; 1928, **51**, 291; Lund and Kenyon, *J. Exp. Zool.*, 1927, **48**, 333; Marsh, *J. Exp. Zool.*, 1928, **51**, 309.

⁴⁵ Francis and Pumphrey, *J. Exp. Biol.*, 1933, **10**, 379.

⁴⁶ Francis, *J. Exp. Biol.*, 1934, **11**, 35.

⁴⁷ Boell and Taylor, *J. Cell. and Comp. Physiol.*, 1933, **3**, 355.

⁴⁸ Taylor, *J. Cell. and Comp. Physiol.*, 1935, **7**, 1.

⁴⁹ Gatty, *Proc. Roy. Soc., A*, 1936, **155**, 704.

⁵⁰ Ponder and Macleod, *J. Gen. Physiol.*, 1937, **20**, 433.

The Composition of the Surfaces in Frog Skin that are Electrically Active.

Few attempts have been made as yet to investigate the composition of the electrically active surfaces in living frog skin. Preliminary experiments with tannic acid⁴⁹ seem to indicate that there is very little exposed protein on the electrically active surfaces of living frog skin; this is to be contrasted with Motokawa's conclusions and those of Amberson and Klein for dead skins. Oxidising agents⁴⁹ like iodine, permanganate, and osmic acid rapidly reduce the potential; the outside of the skin being the more sensitive to the agent both electrically and as a stain. Permanganate has been shown to lower the electrical resistance of the skin and increase its oxygen uptake,¹⁴ these latter tests have not been repeated with the other oxidising agents. These data indicate that a considerable part of the electrical resistance of frog skin is located at some unsaturated oxidisable layer which is nearer the outside than the inside of the skin. Saponin^{49, 50} also destroys the potential and more rapidly from the outside, and this in view of the work of Schulman⁵¹ probably indicates the existence of sterols in the electrically active surfaces in the skin. Fat solvents like ether lower the potential in confirmation of these views.

Work has also been done by several people on the stimulation of nerves of the skin, on the action of physiologically active substances, on the permeability of frog skin which has yet to be proved to show true irreciprocal permeability,* and also on the morphological location of the origin of the potential.

Summary.

A résumé is given of knowledge pertaining to the bioelectrical behaviour of frog skin.

⁵¹ Schulman, *Proc. Roy. Soc., A*, 1936, **155**, 701.

* As opposed to being differently susceptible to injury on different sides by different reagents.

SOME OBSERVATIONS ON SKIN POTENTIALS IN HUMAN SUBJECTS.

By W. F. FLOYD AND C. A. KEELE.

Received 4th March, 1937.

Using the technique and apparatus described by one of us¹ we have measured potential differences between two parts of the skin of human subjects. Fluid contact was made with the subject by means of a pair of reversible cells of the Ag/AgCl/NaCl type the characteristics of which we have discussed elsewhere.²

We have found that there are certain well-defined regions of the skin from which typical variations of potential may be recorded after suitable bodily stimulation. These regions we have termed active regions. The remainder of the body surface does not behave in this way and is termed,

¹ Floyd, W. F., *J. Physiol.*, 1935, **85**, 27, 28P; 1936, **87**, 24P.

² Floyd, W. F., and Keele, C. A., *ibid.*, 1936, **86**, 25P.

therefore, inactive. The active regions comprise the palmar surfaces of the hands and fingers and the plantar and dorsal surfaces of the feet and toes. In order to avoid the difficulties due to the simultaneous occurrence of potential changes at both electrodes, all our observations of the effects of stimulation are made with one electrode connected to an active and the other to an inactive part. Thus, a region at the centre of the dorsum of the left forearm was arbitrarily chosen as the position of the reference (inactive) electrode, with respect to which all potentials are measured. This electrode is connected to the earthed lead of the amplifier and the subject is always at rest upon a couch well insulated from earth.

Resting Potentials.

The circuit conditions employed are such that the current flow through the subject, between the electrodes, is less than 10^{-3} μ A. As is illustrated by the record in Fig. 1 current flow of 0.05 μ A and 0.2 μ A markedly affects the character of the response to stimulation (produced in this case by a single maximal deep breath) indicated in the Figs. by S.

The potentials of inactive regions of the body, measured in this way, varied from +20 mV. to -20 mV. and showed a marked tendency towards bilateral symmetry. The active regions, which we have studied in more detail, are almost invariably negative with respect to the reference electrode.

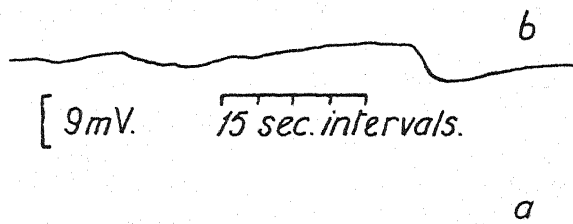


FIG. 2.—(a) Resting potential, skin temp. = 15° C.; (b) resting potential 40 min. later, skin temp. = 26° C., continuous recording in interim. In each case, mean potential = -5 mV.: record taken from tip of second finger, left hand. Subject: C. A. K. Read from left to right.

(with continuous contact) of duration about 15 min. the resting potential of any given part, active or inactive, remains practically constant.

Effect of Skin Temperature on Resting Potential.—Using a thermocouple, we have recorded skin temperatures and have correlated the readings with skin potentials, the area of contact being maintained constant throughout. We can establish no close relation between the magnitude of the potential and the temperature reading. During the course of experiments of long duration we have found the potential to change in either direction with increase of the skin temperature.

There is, however, a very striking change which occurs regularly with increase of skin temperature. The resting potentials, at skin temperatures

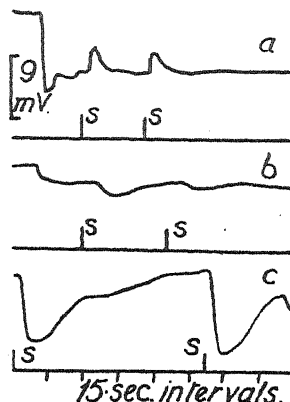


FIG. 1.—(a) Potential responses; (b) responses with mean current flow of 0.05 μ A; (c) responses with constant current flow of 0.2 μ A. Records taken from tip of second finger, left hand. Subject: C. A. K. Read from left to right.

In different subjects the potential of palm and fingers varies from -1 mV. to as much as -50 mV., and occasionally values of the order of -80 mV. have been recorded: in a few cases only we have found potentials of the order of +5 mV. During the course of any one experiment

of the order of 15° C., show practically no spontaneous variations about the resting level. At temperatures in the region of 30° C. there are well-marked spontaneous changes some of which resemble those produced by

TABLE I.*

	A ₁ (7 sq. mm.)	A ₂ (39 sq. mm.)	A ₃ (95 sq. mm.)	A ₄ (270 sq. mm.)
Potential (mV.) .	- 21	- 25	- 23	- 22
Skin Temp. (° C.)	30.5	31.0	30.0	30.5
Potential (mV.) .	- 21	- 20	- 19	- 21
Skin Temp. (° C.)	31.0	31.0	31.0	31.0
Potential (mV.) .	- 30	- 29	- 27	- 28
Skin Temp. (° C.)	25.0	26.0	24.0	30.0

* Subject: C. A. K. active electrode negative with respect to reference electrode.

bodily stimulation. These differences are shown in the records reproduced in Fig. 2.

Effect of Area of Contact on Resting Potential.—We have investigated the relation between the potential of active regions and the area of the fluid contact with the skin and find these

factors to be independent. The areas employed have ranged from less than 1 sq. mm. to 270 sq. mm. In Table I. are given the protocols of three typical experiments in which the potentials were recorded from the tip of the third finger of the left hand.

Occasionally we have observed variations in the readings for these different areas of contact, and we attribute these to the fact that adjacent regions of the skin sometimes differ in potential. In such a case, from a larger area of contact one records the resultant potential of the adjacent parts.

Effect of Electrode Fluid on Resting Potential.—As electrode fluids we have employed sodium and potassium chloride solutions in three different concentrations. We find that the potential of the active region increases in magnitude (numerically) with increase in the concentration of the electrolyte at both electrodes. Typical readings are shown in Table II.

In the case of inactive regions on the arm we do not find regular variations with change of electrolyte concentration for either NaCl or KCl, and the potentials only differ slightly from zero.

TABLE II.

Electrolyte.	Concentration (grm. p.c.)	Potential (mV.).
NaCl	0.09	- 1
	0.9	- 10
	9.0	- 18
NaCl	0.09	- 5
	0.9	- 16
	9.0	- 26
KCl	0.09	+ 5
	0.9	- 5
	9.0	- 15

Potential Changes Produced by Stimulation.

Changes in potential are produced by many different forms of bodily stimulation, such as a sudden loud noise (motor horn), an electric shock and the like. We have used several such stimuli, but now employ mainly a single maximal deep breath because we find that repeated use of this stimulus gives the more uniform results. We use the term "potential responses" to describe these changes in potential. The potential usually, but not invariably, returns to the original level after the effect of stimulation has passed. The responses may be negative or positive with respect to the resting level and may consist of one or more waves: in some cases

they are complex in character and comprise both positive and negative waves in succession. The records shown in Fig. 3 illustrate this. We have recorded several different types of potential response from the same subject at different times.

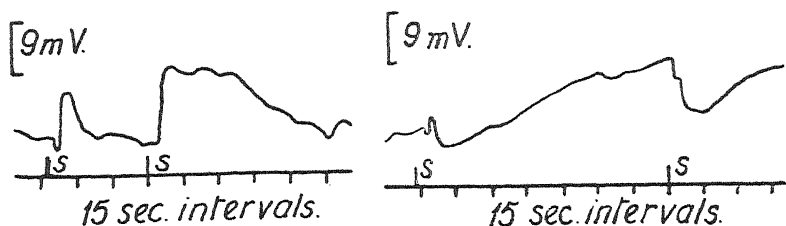


FIG. 3.—Typical potential responses, stimulus a single maximal deep breath. Both records taken from palmar surface of left hand, 45 mins. interval between them. Subject: P. B. W. Read from left to right.

Effect of Skin Temperature on Potential Response.—Apart from the spontaneous activity of active regions already mentioned, we are unable to demonstrate any close relation between skin temperature and the character of potential responses. In the same subject we have found, during the course of the same experiment, (a) an increase in the amplitude of responses from one finger tip, and (b) no change in the amplitude of responses from another finger tip, with an increase of skin temperature from 15° C. to 28° C. in each case. We find, also, no discernable differences in the shape and time relations of comparable responses, with change of skin temperature.

Effect of Area of Contact on Potential Response.—Like the resting potentials the potential responses are found to be independent of area of contact.

Summary.

Potentials have been recorded from different parts of the body surface relative to a fixed point. Certain regions, termed active, show potential changes following suitable bodily stimulation. The effects on skin potentials of skin temperature, area of electrode contact, and electrode fluid are described.

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THE ORIGIN OF BIOELECTRIC PHENOMENA.

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Received 26th February, 1937.

According to Bernstein's well-known theory (developed by Tschermak) action currents arise as a consequence of changes in the ionic permeability of certain membranes. As a result of these changes ions which were previously unable to diffuse through the membrane become free to do so, and so lead to a change in electrical potential.

How this change in ionic permeability arises was not considered by the theory. It is now possible, however, to define the conditions which may lead to such a change. The conversion of a membrane permeable to uncharged particles or to cations, into one permeable to anions, can only occur as a result of chemical change in the membrane itself, or of a variation in p_H of the surrounding medium. Michaelis has shown that protein membranes, in a medium whose p_H corresponds to their isoelectric point, are not selectively permeable to ions: in an alkaline medium, however, they become permeable to cations, and in an acid medium to anions.

The cause of the change in permeability postulated by Bernstein's theory, must therefore be ascribed to a preceding chemical reaction. Such reactions, however, can themselves give rise to action currents without a subsequent change in permeability. It is therefore unnecessary, to suppose, with Bernstein, that a change in permeability is the common cause of bioelectric phenomena.

Whenever reactions proceed in the organism such that ions are formed or disappear locally, *e.g.*, esterification or saponification, the formation or splitting of amides, liberation or destruction of acetyl choline or lactic acid, etc., measurable potential differences will arise, if the tissues bounding the site of reaction possess different ionic selectivities in the directions of the two electrodes. If the ionic concentration is increased, the cations will diffuse through the tissue permeable to cations (acidic protein), and will produce therefore a positive charge on the electrode in the neighbourhood: correspondingly the anions will pass through the tissue permeable to anions, so that the electrode in this direction will become negative. If the ionic concentration is reduced (instead of being increased) the effect will be reversed.

We believe that action currents are simply a necessary accompaniment to the chemical reactions assumed to take place in any organ during activity. It is possible that changes in permeability also occur as a consequence of these reactions, but such must be regarded as secondary phenomena.

The structure of the electric organ in certain fishes has been investigated, in order to ascertain whether the production of electricity can be explained in terms of the microscopic structure of the organ and the ideas here developed. A single columnar unit of the organ is built up from the lamellæ. At my suggestion Professor Guyénot of the Zoological Laboratory, Geneva, examined the staining reactions of the organ with a suitable mixture of eosin and methylene-blue. It was found that each lamella is composed of two sheets, the dorsal sheet being stained by the basic dye methylene-blue and the ventral sheet stained by the acid dye eosin. The dorsal sheet must therefore be permeable to cations, the ventral to anions.¹ Each lamella can be considered as a galvanic element, which produces current, if the ionic concentration in the interior of the lamella is increased as a result of a stimulus. The dorsal surface will be charged positively. The organ can be regarded as a series of these elements, the total potential difference being the sum of all the individual potential differences.

It is suggested that the action current of a muscle fibre may be explained in terms of chemical changes in the sarcoplasm, and of the morphological arrangement of the basic and acidic components (respectively permeable to anions and cations). Thus it is known that

¹ *Naturwiss.*, 1926, 14, 33.

the fibrils are stained by acid dyestuffs, *i.e.*, they contain basic protein and are therefore permeable to anions. If ions are set free in a certain region of the sarcoplasm, these in diffusing will encounter fibrils in directions at right angles to the fibre axis, but sarcoplasm in the direction of the axis. Since the fibrils are preferentially permeable to anions the rate of movement of these will be more rapid in directions at right angles to the fibre axis than in the direction of the axis, and a negative variation in potential (the action current) will be produced in this region, as long as the ionic concentration is increased.

The origin of the action current in nerve may be explained in a similar manner. It is known that the axial fibre contains neurofibrils which are stained by acid fuchsin and are therefore permeable to anions. If, as a consequence of the stimulus, ions are momentarily set free and then disappear, and if this cycle of events is propagated along the fibre, a negative variation in potential will be observed at the laterally placed electrode, since the diffusing anions will encounter basic fibrils in the lateral direction and will therefore diffuse more rapidly in this direction than in the direction of the axis. For further details, see *Helv. Chim. Acta*, 1937, **20**, 634.

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GENERAL DISCUSSION.*

Dr. S. L. Cowan (*London*) introducing his paper said: I have drawn attention to the fact that both in frog muscle and in crab nerve the injury potential ordinarily observed is only one-half to two-thirds of that which would be expected were it assumed that the ratio $[K_{\text{inside}}]/[K_{\text{outside}}]$ is the only variable concerned. There are, however, three additional factors which may explain the discrepancy between the observed and calculated potentials: (1) short-circuiting by connective tissue and interstitial fluid; (2) a potential due to asymmetry of the membrane, and acting in the opposite sense to that of the injury potential; (3) the "concentration effect" which has been discussed by Professor Kurt Meyer and by Doctor Teorell. At present there are few measurements on muscle or nerve which would enable us to estimate the relative magnitudes of the three factors. In muscle at least, the second may prove to be more important than has been anticipated, for recently Francis † has estimated the asymmetry potential of the membrane to be 10-20 millivolts. I would like to point out also, that Professor Meyer's and Dr. Teorell's calculations show us that replacement of the interstitial fluid by a non-electrolyte solution would upset the Donnan equilibrium obtaining at the outer surface of a nerve or muscle membrane, and hence the boundary potential there. Consequently, unless this boundary potential can be shown to be negligibly small, it is not valid to estimate the short-circuiting due to the interstitial fluid simply by replacing this fluid with a non-electrolyte solution and then measuring the attendant change of injury potential.

Dr. J. H. Schulman (*Cambridge*) said: The following simple calculation shows that considerable salt concentration differences in a cell can be obtained by other forces than "osmotic forces."

Imagine a layer of orientated polar groups \pm composed for example of carboxyl dipoles ($-\text{COOH}$) at an interface of 1 c.c. N HCl solution and each polar group were to adsorb one H^+Cl^- from the solution, one would require approximately 200 mg. of oleic acid to change N HCl \rightarrow 1/2N HCl.

* On 6 preceding papers.

† Francis, W. L., *Proc. Roy. Soc., B*, 1937, **122**, 140.

200 mg. oleic acid requires about 10^6 cm² of surface area, hence adsorption by *one* layer of orientated molecules could change the concentration of N HCl solution to $1/2N$ HCl solution if the acid solution is 100 Å in depth from the orientated polar layer. Therefore if a depolarising system is possible at the interface to remove the adsorbed ions or molecules, a mechanism for changing the concentrations of salts or other adsorbable material is available. By assuming a mixed layer of lipid protein molecules one would have many more polar groups per unit area for adsorption purposes, than for the example given above, hence salt concentrations in dimensions as found in the nerve cell could be radically altered by a simple depolarisation mechanism or renewal of material at an interface. It is hoped by a moving film technique to demonstrate experimentally that large concentration changes can be made by other methods than diffusion.

Dr. T. Teorell (*Uppsala*) said : (1) It may perhaps be somewhat misleading to speak of negatively or positively charged membranes as being "cation or anion permeable," as has been done repeatedly in this discussion. Such charged membranes still have to allow equal numbers of cations and anions to pass through, otherwise a space charge of free electricity would develop. The effect of the charge on a diffusion membrane is certainly a change in the velocity of electrolyte flow through the membrane and also separation effects on the ions of the water ("membrane hydrolysis"). However, a theory for the velocity of ionic or electrolyte *flux* across uncharged or charged membranes is still lacking.

(2) In connection with the discussion on various bioelectrical potential changes, it may be of interest to point out that potentials can be produced during the expansion of thin non-aqueous films interposed between electrolyte solutions.¹ Such a potential can vary in different ways depending on the nature of the interfacial film, the rate of expansion and several other factors. It can easily amount to several tens of millivolts. As potentials can be observed also in cases where the electrolyte solutions inside and outside of the film are identical, they have to be ascribed to some asymmetry in the two interfaces. Frequently a sudden "break down" of these asymmetry potentials can be observed when a certain stage of thinness of the interfacial films is attained. *Stepwise* changes in the electrical conductivity when the non-aqueous layer grows thinner is often characteristic behaviour of such films.

Dr. W. Wilbrandt (*Bern*) said : Working in Professor Höber's laboratory with organic ions I found² that the action of potassium on the resting potential of nerves is not as unique as it seemed before. Organic cations such as dialkylammonium, tetraalkylammonium, and guanidine show a reversible lowering effect on the resting potential, which, in some cases, for instance with diamylammonium, is about as strong as that of potassium.

It was also found, that anions are not quite indifferent. Both inorganic anions (SCN, NO₃) and organic anions (lactate, pyruvate, acetate, propionate, butyrate) show a slight but definite raising effect on the resting potential, which is also reversible. The nerve membrane, therefore, seems not to be exclusively cation-permeable.

It seems possible, that at least the after potentials are due to the formation in the metabolism of organic ions.

Professor A. V. Hill (*London*) said : No extensive chemical change can be the basis of transmission of the nerve impulse, since the immediate rise of temperature associated with the passage of a single impulse in medullated nerve is only a small multiple of 10^{-8} degrees C. On the other hand, some chemical change undoubtedly does occur, and in the recovery process following activity oxygen is consumed and a larger amount of heat given out.³

¹ *Nature*, 1936, **137**, 994.

² *J. Gen. Physiol.*, 1937, **20**, 519.

³ See A. V. Hill, *Chemical Wave Transmission in Nerve*, Cambridge University Press, 1932.

It is unnecessary to invoke any special mechanism of the "action potential" associated with activity: this is smaller than, but of the same order of size as, and might under special circumstances be a large fraction of the resting ("injury") potential; it could most simply be explained as due to a momentary change of the surface in the nerve across which normally the resting potential exists.

Mr. J. J. Bikerman (*Manchester*) said: Professor Blinks has stated that the capacity of plant membranes is rather a polarisation capacity than a static one. Now, if a porous membrane (*i.e.* not of the type "oil" between two water layers) possesses an electrokinetic potential ζ , it is polarisable. The ratio of its capacity for $\zeta \neq 0$ to that for $\zeta = 0$ (for instance at the isoelectric point) is given¹ by the expression

$$\frac{\text{capacity at } \zeta \neq 0}{\text{capacity at } \zeta = 0} = \frac{i_{\omega} + i}{i},$$

where i_{ω} is the surface current and i the current flowing through the bulk of the pores. As i_{ω} is proportional to the circumference, and i to the cross-section of a pore, the polarisation capacity of a membrane may be changed simply by changing the radius of its pores. In organic membranes it can be done by swelling. The swelling is a slow process; that may be the explanation of the slow establishment ("up to a second or more") of the final capacity in Professor Blinks' experiments.

Dr. R. B. Dean (*Cambridge*), in introducing his paper with Mr. Gatty said: First we wish to correct an error in the last sentence of our paper. Professor Krogh has of course demonstrated active transport of chloride ions and sodium ions across the skin of an intact living frog.

Our paper gives a resumé of work done on the bioelectric properties of frog skin, and points out some sources of error in interpreting these phenomena.

The reversible drop in potential on replacing Na in Ringer by K is accompanied by an increase in the electrical conductance which is about 700 per cent. greater with sixty times the usual K content, *i.e.*, is nearly Na free. This increase in conductivity cannot be attributed solely to the greater mobility of K ion, because high K on one side lowers the potential regardless of the direction of the K gradient. High K Ringer on both sides reduces the potential to zero.

Also when a dilute solution free of Na, such as KCl containing as much K as does Ringer, is placed outside, the potential goes to negative values. Several killing agents make this potential more negative, indicating the destruction of a respiratory potential. High K-substituted Ringer inside may make the potential more negative, but more often it changes the potential from -30 to $+30$ millivolts. The expected change due to the K gradient is in the opposite direction. These phenomena lead us to suppose that K increases the permeability of negative ions, perhaps by specific absorption on pores in the skin.

The very high resistance of the skin when dilute solutions are outside (about 10 times that of the skin in Ringer) is destroyed by permanganate ion, saponin or other killing agents. From this we conclude that the high resistance is not due entirely to washing out of salts from the skin pores but may be a protective mechanism to enable the frog to maintain its osmotic pressure in dilute solutions.

Dr. T. Teorell (*Uppsala*) said: One result obtained by various workers on the frog skin potential² is the following: When the potential across a frog skin is measured with the same salt on both sides and the solution on *one* side is diluted, a typical change in the P.D. can be observed. With moderate dilutions an increase in the P.D. occurs, but when applying still more diluted solution a potential maximum is reached and a

¹ J. J. Bikerman, *Koll. Z.*, 1935, **72**, 100.

² Steinbach, Dean and Gatty, etc.

decrease of the P.D. takes place, it may even change sign. No satisfactory explanation of this behaviour seems to have been given as yet. Therefore, it is interesting to note that a similar type of curve could be theoretically predicted if we regard the frog skin P.D. to be a "mixed membrane potential." The concept of the "mixed" potential is a development and refinement of some ideas first presented by Wilbrandt.¹ The theory was published by me in 1935,² but was also worked out independently by Meyer and Sievers, in 1936.³ The chief points are the following:

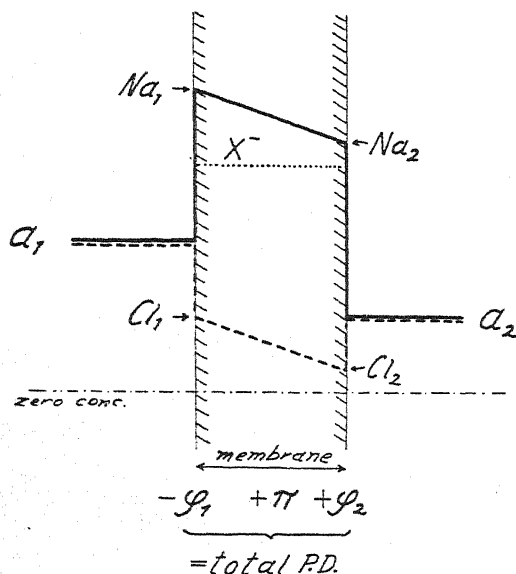


FIG. 1.

Consider a membrane which carries electrical charge. This charge may be due to an electrolyte character of the membrane substance itself, or the charge may be caused by "adsorption" or polar groups, etc. For simplicity we may represent the membrane by X^- behaving as an *immobile*, negative ion uniformly distributed within the membrane. Then NaCl is placed on both sides of the membrane. What will happen? The very beginning is hard to account for, but ultimately an ionic distribution according to the sketch (Fig. 1) may be attained. Two Donnan distributions are obtained, one at each phase boundary (where $Na > Cl$). At the

same time two potential jumps appear, ϕ_1 and ϕ_2 (each being of the form $58 \cdot \log \frac{Na_{bulk}}{Na_{membr.}}$). Besides this two boundary potentials, there must arise a common diffusion potential, π . This can be easily calculated according to Henderson's formula, because all concentration gradients are likely to be linear. The complete formula for the total membrane P.D., i.e., the "mixed" potential, is written

$$\text{Total P.D.} = 58 \left[\underbrace{\log \frac{a_1 \cdot Na_2}{a_2 \cdot Na_1}}_{\text{Donnan}} + \underbrace{\frac{u-v}{u+v} \log \frac{Na_1(u+v) - X \cdot v}{Na_2(u+v) - X \cdot v}}_{\text{Henderson}} \right]$$

Here a_1 and a_2 are the bulk concentrations of the NaCl, Na_1 and Na_2 the boundary concentrations due to the Donnan distribution and u and v the mobility of Na and Cl. If X denotes the "membrane concentration," then Na_1 (and Na_2) can be evaluated from Donnan equations $a_1 \cdot a_1 = Na_1 \cdot Cl_1$ (after substitution of Cl_1 by $(Na_1 - X)$ one finds that $Na_1 = \sqrt{a_1^2 + 0.25 X^2} + 0.5 X$).

If a_1 , the salt concentration on the one side, is kept constant, and a_2 varied in the formula given, results will be obtained as given in the table on next page.

¹ J. Gen. Physiol., 1935, 18, 933. ² Proc. Soc. Exp. Biol. Med., 1935, 33, 282.

³ Helv. Chim. Acta, 1936, 19, 649.

When these values are plotted the course of the curve is of the same type as was observed in some corresponding experiments on frog skin. The course may be shifted somewhat if the membrane "concentration" X is not the same at both interfaces.¹

Dr. G. S. Adair (*Cambridge*) said: In the experiments of Floyd and Keele on the skin potentials in human subjects a small flow of current affected the responses. In a system where one electrode was on the slightly abraded skin and a second electrode was in the stomach,² the potentials were not affected by a slight flow of current, so that they could be measured with a potentiometer and a moving pointer galvanometer.

Dr. S. L. Cowan (*London*), in reply, said: I have made no experiments on the depolarisation of *Maia* nerve by acetylcholine, but Dr. Bernhard Katz³ permits me to mention some experiments of his with *Carcinus* nerve. In these he was able to set up trains of propagated impulses in the nerve by localised application of 1/10,000 acetylcholine solution. It is possible to set up similar trains of impulses by the localised application of potassium chloride solution to *Maia* nerve.

Membrane "concentration" $X = 1$; Conc. of NaCl inside $a_1 = 100$;
Mobility ratio Na : Cl, $u : v = 0.63$.

Conc. of NaCl Outside.	Potentials (in Millivolts).			
	Donnan.		Henderson.	Total P.D.
a_2 .	ϕ_1 .	ϕ_2 .	π .	"Mixed" P.D.
100	± 0	0	0	+0
10	-0	+ 1.2	-13.2	-12.0
5	-0	+ 2.2	-17.4	-15.2
1	-0	+12.2	-26.4	-14.2
0.5	-0	+22.2	-29.4	- 7.2
0.1	-0	+58.0	-31.6	+26.4

In muscle and in nerve the resting potentials are to be regarded, for short times at any rate, as steady state phenomena closely dependent on metabolism and on ionic environment. A change of ionic environment which reduces the potential results also in a change of metabolism. Therefore, it is not to be expected that the relations observed between injury potential and ionic environment will accord exactly with formulæ which neglect the effects of metabolism.

Disregarding the question of metabolism, we have no satisfactory evidence as to the thickness of the membranes bounding the physiologically active surfaces of muscle and of nerve. It may be that they are too thin for the Meyer-Teorell method of calculation to be applied without modification. In any case the sieve-like property of the membrane is a very important factor. To my earlier remarks I would like to add the suggestion that alteration of the solution bathing the external surface of a muscle or nerve fibre may also alter the size of the pores of the sieve (see Netter, 1927; Höber and Strohe, 1929).

In reply to **Dr. Wilbrandt** (*communicated*): The action of tetraethylammonium or of guanidine ions upon the injury potential of nerve may also involve: 1. partial depolarisation as a result of "spontaneous" activity; 2. an effect on the properties of the membrane.

¹ Cf. also p. 1141.

² Adair and Goodman, *J. physiol.*, 1936, 87, *Proceedings* 12, Quigley (*in press*).

³ Katz, B. (1937). *Personal communication*. See also part of letter from Katz to Bacq quoted in Bacq, Z. M., *Arch. int. Physiol.*, 1937, 44, 174.

Dr. Ing and I¹ found evidence that tetra-ethylammonium ions cause the response of crab nerve, or of frog nerve, to become repetitive. Dr. Walter and I² have found that tetra-ethylammonium ions reduce the rheobase, and prolong the time-constant of accommodation³ of frog nerve. "Spontaneous" activity is the limiting result of these changes, which may be reversed by the washing out of tetra-ethylammonium ions, or by the addition of calcium ions. A possible explanation of the results is that tetra-ethylammonium ions displace calcium ions from a position that they normally occupy at the outer surface of the nerve membrane.

I have found⁴ that guanidine also prolongs the time-constant of accommodation, and reduces the rheobase of nerve. Again, these changes can be reversed by calcium ions.

Dr. R. B. Dean (*Cambridge*), in reply, said: Another error needs correcting in my paper. Steinbach¹⁴ got indications of opposing potentials when the outer solution was dilute and he states this on page 8 of his paper but implies the opposite on page 24. The later statement was referred to when saying "though he states they prove the contrary conclusion." (see p. 1042).

Professor Kurt H. Meyer (*Genthod Geneve*), in reply, said: I think it is time to replace the signs + and —, so dear to the physiologist, as well as the Helmholtz double layer, by more accurate concepts. Positive and negative charges in living systems only occur bound to atoms or groups of atoms as *ions*. All electrical phenomena in organisms, and in particular the conduction of electricity, potential differences and polarisation, depend on the arrangement and mobility of such ions. Only in the case of very rapid changes in potential, as for example, in the phenomena displayed under high frequency current, have asymmetrical distributions of charge in groups of atoms (dipoles) to be taken into account.

From these considerations questions arise as to the nature of these changes in arrangement and mobility of ions, which are the cause of potential changes and which have been discussed in my paper. One of these questions concerns the rôle of potassium. In this case our knowledge of the structure of the potassium ion enables us to say the following: potassium is only present as potassium ions, which can neither appear or disappear, since the electron-shell of the potassium ion is almost the same as that of argon and similarly stable, so that the potassium ion cannot be masked in forming a complex with any other molecule. Only "free" potassium ions are known, whose mobility may be influenced by fields of surrounding anions, by membranes, or by the nature of the solvent. This explains the results obtained by Hill and Kupalov⁵ and Bozler and Cole,⁶ who showed that all the potassium present in muscle is present as potassium ion. Every event involving the presence of potassium, *e.g.*, the escape of K ions from the muscle during contraction, presupposes a chemical change in the environment of the ions (in this case, the membrane holding back the ions becomes more permeable). This reversal in permeability, which itself must have a chemical origin, may be explained (in terms of the scheme proposed by Michaelis) as a consequence of a shift in the p_H of the medium towards the alkaline side—which von Murlat has actually shown to take place during muscular contraction.

The restriction valid for the case of K⁺ does not apply to organic ions, which may appear or disappear as a result of chemical reactions; nor does it apply to numerous inorganic ions such as PO₄' or Cl'. These may be masked by esterification and set free by saponification.

It has also been suggested that the changes in permeability of the membrane might depend on changes in the degree of swelling of the

¹ S. L. Cowan and H. R. Ing, 1935. *J. Physiol.*, **84**, 90.

² S. L. Cowan and W. G. Walter, 1937. *In course of publication.*

³ A. V. Hill, 1935.

⁴ *Unpublished.*

⁵ *Proc. Roy. Soc., B*, 1930, **106**, 445.

⁶ *Cell. Comp. Physiol.*, 1935, **6**, 229.

membrane, but this change also can only occur as a result of chemical processes. Thus in all cases the search for an explanation of electrical phenomena in muscle and nerve leads back to chemical events in the metabolism of these structures. It has been my object to show that in all probability a direct connection exists between these processes and the phenomena of action-currents.

THE ACTION OF NARCOTICS ON ENZYMES AND CELLS.

BY A. J. CLARK.

Received 2nd March, 1937.

Overton and Meyer in 1899 showed the remarkable parallel between the differential oil/water solubility of aliphatic compounds and their narcotic action on cells. This was one of the first attempts to explain the laws regulating the action of drugs on cells. The difficulty of this subject is well illustrated by the fact that there is still no general agreement as to whether the action of aliphatic narcotics depends on their oil/water distribution. The subject in the intervening years has accumulated a huge literature but fortunately this was summarised by Winterstein¹ and full references will only be given to work mentioned, which is subsequent to this date.

The fact that no certainty has yet been reached on this subject seems to the writer a striking confirmation of the general thesis that the living cell is so complex an organisation that at present we cannot hope to obtain formal proof of the manner in which its functions are modified by drugs and must be content with weighing probabilities. At the present date there are two important rival hypotheses regarding the mode of action of aliphatic narcotics on living cells: (1) that the cell surface owes its properties to its lipine content, and that narcotics act by dissolving in these lipines, owing to their oil/water distribution coefficient, and thus change the cell surface properties; (2) that narcotics are adsorbed on the cell surface and cover it with an inert layer. The evidence relevant to this controversy is too extensive to permit of even a full summary but the following points appear to the writer to be of outstanding importance:—

(i) The relation between the concentration of narcotics and their action is nearly linear, provided that the action produced is of a graded as opposed to an all-or-none character. A relation of this form is comparatively rare.

(ii) In the case of homologous series of aliphatic compounds, *e.g.*, alcohols, urethanes, etc., the pharmacological activity increases about threefold with each addition of a carbon atom. This rule is only true of straight-chain compounds, but in this case it holds over a remarkable range of chain length and pharmacological activity.

The hypothesis that these outstanding characteristics are dependent on oil/water distribution can most simply be tested by determining whether they are dependent on the presence of lipines or whether they occur with lipine-free systems.

¹ Winterstein, H., *Die Narkose*, 2te. Aufl. (Springer, Berlin, 1926).

The poisoning of inorganic catalysts such as metal surfaces by narcotics has been studied extensively but comparisons between such catalysts and living cells are unsatisfactory because the activity of the catalysts is believed to depend on active atoms which occur in rigid surfaces but are unlikely to occur in protoplasmic surfaces.

The study of enzyme poisoning is much more satisfactory because so many of the functions of living cells are carried out by enzymes. In some cases it is even possible to compare the action of narcotics upon purified enzymes and upon the same enzymes *in vivo*. Narcotics inhibit many but not all enzymes, and their inhibitory action is not markedly selective or specific. For example ethyl urethane inhibits a large number of enzymes and the concentration needed to produce inhibition is similar in most cases. Schürmeyer (1925) showed that purified invertase is not inhibited by ethyl alcohol, but that if globulin was added then alcohol produced inhibition. This suggests that the inhibition depends upon the active group of the enzyme being fixed to particles of colloidal dimensions, and is in accordance with the hypothesis that the inhibition is due to an adsorption process.

Concentration-Action Relations found with Enzymes and Cells.—The relation between the concentration of narcotic and the amount of inhibition produced in the activity of partly or completely purified enzymes is in many cases nearly linear, *e.g.*, inhibition of invertase (Meyerhof 1914); inhibition of serum-lipase (Rona and Lasnitzki, 1925). In some cases the concentration-action curves are intermediate between a linear relation and an adsorption curve, *e.g.*, inhibition of succino-hydrogenase by alcohols (Grönvall, 1923) and by urethanes (Svensson, 1923).

Linear concentration-action relations were found by Lipschitz and Gottschalk (1921) who measured the action of narcotics upon the power of muscle pulp to reduce di-nitrophenol. This represents an intermediate system since the muscle pulp contained lipines but all the living cells were disorganised.

The majority of observers who have measured the action of narcotics on the enzymatic activity of living cells have found nearly linear concentration-action relations, *e.g.*, inhibition of oxygen uptake of bird's red blood corpuscles (Warburg, 1914), and of sea urchin eggs (Meyerhof 1917) and of bacteria (Meyerhof, 1916). In some cases adsorption curves have been obtained, *e.g.*, inhibition of carbon dioxide production of *Chlorella* (Warburg, 1920). A concentration-action relation which is nearly linear, but slightly curved so as to be intermediate between a linear and an exponential relation has been found with a large variety of tissue activities, *e.g.*, inhibition of reflexes in spinal cat (Storm van Leeuwen, 1913); inhibition of contraction of tortoise heart (Vernon, 1911-12), of frog heart;² inhibition of oxygen uptake of frog's heart.³

In the case of cardiac oxygen consumption it may be noted that the study of the time relations of the action, shows that the inhibition of muscular contraction occurs much too rapidly for it to be caused by oxygen lack. Consequently the depression of oxygen consumption is probably secondary to the depression of the contraction process, and therefore this cannot be considered as an example of an effect due to the inhibition of an enzyme. This is an example of the difficulties that arise in the interpretation of the response of systems as complex as living cells.

The author's interpretation of the striking resemblance found between the concentration-action relations of narcotics acting on systems as different

² (a) Clark, A. J., *Arch. int. Pharmacodyn.*, 1930, **38**, 101. (b) Clark A. J., and White, A. C., *J. Physiol.*, 1928, **66**, 185. (c) *ibid.*, 1930.

³ Clark, A. J., *Mode of Action of Drugs on Cells* (Arnold & Co., London, 1933). Kernot, J. C., and Hills, H. W., *Z. physiol. Chem.*, 1933, **222**, 11.

as purified enzymes and a cat's central nervous system, is similar to that advanced by Winterstein,¹ namely that the adsorption of narcotics on a surface usually follows Langmuir's formula and there is an exponential relation between concentration and amount adsorbed. If more than half the total adsorption possible is required in order to produce full inhibition of an action then an exponential relation is seen between concentration and action. If, however, the full action is produced when the surfaces are less than half saturated then the concentration-action relation approximates to a linear relation, although really it is a portion of an exponential curve.

The author has shown³ that the action of narcotics in lowering the air/water surface tension follows, over the range of concentrations of physiological interest, a nearly linear relation exactly similar to that obtained with living cells. The linear concentration-action curve usually is adduced as a proof of the action being due to differential solubility but this leaves the non-linear relation unexplained and does not explain the resemblance between the actions on enzymes and on living cells whereas the adsorption hypothesis accounts for these facts.

TABLE I.

Actions and Authors.	Molar Concentration Producing Action.			Ratio [C ₂ H ₅ OH]/[C ₁₀ H ₂₁ OH].
	Ethyl Alcohol.	<i>n</i> -Amyl Alcohol.	<i>n</i> -Decyl Alcohol.	
50 per cent. inhibition frog's ventricle (Clark, 1930)	0.65	0.02	0.00003	22,000 (3.5 ⁸)
Just measurable inhib. frog's heart (Mezey and Staub, 1935)	0.087	0.0018	—	—
Narcosis of tadpoles (Meyer and Hemmi, 1935)	0.33	0.007	0.00001	33,000 (3.7 ⁸)
Equal reduction air/water surface tension . .	0.5	—	0.00009	5,500 (2.9 ⁸)

Law of Homologous Series.—The regularity with which the pharmacological activity of narcotics increases with increasing length of carbon chain is a very striking phenomena. It is seen with many series, but the evidence in the case of the normal alcohols is most complete. Table I. shows the equi-narcotic and iso-capillary concentrations of ethyl and *n*-decyl alcohols.

There is a larger amount of evidence for the range ethyl to *n*-heptyl alcohol. Fühner (1912) measured the iso-narcotic concentrations of ethyl and *n*-heptyl alcohol on 23 different species of water-living animals ranging from protozoa to amphibia. The ratios (C₂H₅OH) (C₇H₁₅OH) ranged from 2.98⁵ to 4.57⁵. Tilley and Schaffer⁴ measured the lethal action of alcohols on bacteria and found the ratio between the minimum lethal concentrations of ethyl and *n*-heptyl alcohols to be 3.3⁵.

Other values for this ratio can be obtained from the results of the authors referred to in Table I. The general result is that there are 27 different estimations of the biologically active concentrations of ethyl and *n*-heptyl alcohols, and 21 of these show values between 3.2⁵ and 4.0⁵, with an average of 3.6⁵.

⁴ Tilley, F. W., and Schaffer, J. M., *J. Bact.*, 1926, 12, 203. Wertheimer, E., *Protoplasma*, 1934, 21, 521.

The author found the following ratios for isocapillary concentrations: ethyl/heptyl = 3.8^5 ; ethyl/decyl = 2.9^8 . With regard to these results it may be remarked that the experiments with the alcohols higher than *n*-heptyl are unsatisfactory in that it is doubtful if a true solution is obtained even in the very low concentrations which are biologically active. Probably even in these concentrations the alcohols are present as a colloidal suspension.

Warburg and Wiesel (1912) showed that with alcohols or with urethanes the same ratios for equiactive concentrations of different members of homologous series were obtained for the depression of the oxygen consumption of red blood corpuscles and for the enzyme activity of lipine-free systems such as acetone-extracted yeast. Meyer and Hemmi⁵ pointed out that the concentration of alcohol needed to inhibit the yeast was ten times that needed to narcotise tadpoles but was similar to that required to precipitate nucleo-proteins.

This criticism is, however, of doubtful significance, for example the Table shows that Mezey and Staub's⁶ figures for the threshold inhibitory concentrations of alcohol inhibiting the frog's heart are about 1/10 those found by the author to produce 50 per cent. inhibition of the frog's ventricle. The latter effect was, however, freely reversible and there are no grounds for considering the two effects different in character.

Various authors have measured quantitatively the inhibition of enzymes by homologous series of narcotics, *e.g.*, alcohols on partly purified invertase (Meyerhof, 1917), alcohols on fermentation by living yeast (Wertheimer 1934), urethanes on acetone-extracted yeast (Warburg and Wiesel, 1912) and on living yeast (Dorner, 1912). Alcohols on succinic dehydrogenase (Gronvall, 1923), urethanes on the same (Svensson, 1923), alcohols on liver lipase (Kemot and Hills, 1923), alcohols and urethanes on power of muscle pulp to reduce dinitrobenzol (Lipschitz and Gottschalk, 1921).

In all cases similar ratios between the activity of different members of homologous series have been found. The resemblances between the ratios found with enzymes and with cells are very striking but are not exact. For example, the ratio between ethyl and *n*-amyl alcohol as measured by inhibition of liver lipase was estimated as 23 and 29 (2.8^3 and 3.1^3) whilst the corresponding ratios for living cells average 3.6^3 . Unfortunately inaccuracies of this type are characteristic of pharmacological evidence and can only be avoided if extraordinary precautions are taken to eliminate errors due to individual variation, etc.

The chief objection to the adsorption theory is that the correspondence between physiological action and capillary action does not hold when different series are compared. For example the isocapillary concentrations of *n*-amyl alcohol and of chloral hydrate are 0.018 and 0.4 molar, a ratio of 1 to 20. Chloral hydrate has, however, an action on living cells about equal to that of amyl alcohol.^{2a, 6}

There are, however, a few observations on the action of chloral hydrate on enzymes which show that its activity approaches that of amyl alcohol. For example Svensson (1923) found a 50 per cent. inhibition of succinic dehydrogenase with 0.1 molar chloral hydrate and with 0.12 molar *i*-butyl urethane, whilst Gronvall (1923) found the same effect with 0.4 molar *n*-butyl alcohol. These results indicate that the equiactive molar concentration of *n*-amyl alcohol would lie between 0.1 and 0.2 molar, which indicates that the activity of chloral hydrate is equal or slightly more than that of *n*-amyl alcohol.

Lipschitz and Gottschalk (1921) found equal inhibition of dinitrophenol reduction by pulp of frog's muscles with 0.183 molar chloral hydrate and 0.088 molar *i*-amyl alcohol.

⁵ Meyer, K. H., and Hemmi, H., *Biochem. Z.*, 1935, 277, 39.

⁶ Mezey, K., and Staub, H., *Arch. exp. Path. Pharmac.*, 1935, 180, 12.

Any explanation of the striking divergence between the *isocapillary* and *isonarcotic* ratios of *n*-amyl alcohol and chloral hydrate must, therefore, also account for an equal divergence between the *isocapillary* ratio and the ratio between the concentrations *isoactive* upon enzymes. The same argument applies to the action of chloroform which presents the same difficulty as does that of chloral hydrate.

Quantitative Data.—The evidence available regarding the uptake of narcotics by cells is on the whole in favour of adsorption, but is in no way decisive. With low concentrations of ethyl alcohol⁷ the concentration in a perfused tortoise heart was similar to the concentration in the perfusion fluid, but when the concentration in the fluid rose to 0.5 molar, which was sufficient to produce 50 per cent. inhibition of the ventricle, the heart content of alcohol was only 0.25 molar.

In the case of the higher alcohols (*n*-heptyl to *n*-dodecyl) Clark^{2a} calculated the amount fixed by the frog's heart when an equal inhibition was produced. The *isoactive* concentration in the fluid ranged from 0.0007 molar *n*-heptyl alcohol to 0.000006 molar *n*-dodecyl alcohol. The amount of alcohols fixed by the heart appeared, however, to be nearly constant and equal to 0.003 molar. This result accords with the hypothesis that the alcohols act by covering some surfaces in the cells, but it would agree equally well with Meyer's hypothesis than an equal narcotic effect is produced when a certain concentration of narcotic is attained in the cell lipines.

Drug Antagonism.—Warburg showed that narcotics interfered in a similar manner with the action of cyanides on cells and on the inorganic catalyst, blood charcoal. This he regarded as strong evidence in favour of the adsorption hypothesis. His results have been confirmed by Lipschitz and Gottschalk (1921). It has already been pointed out that the active groups of inorganic catalysts must differ widely from the active groups of enzymes and hence the relation between the action of narcotics on blood charcoal and on cell oxidases is uncertain. A further objection is that a system in which two drugs act on an enzyme contains a large number of variables. For these reasons the results quoted are not altogether conclusive but they accord very well with the hypothesis that narcotics act by adsorption and are difficult to explain on any other hypothesis.

Discussion.

The action of narcotics on cells presents a number of striking features. These can be explained most easily by the hypothesis that narcotics are adsorbed on surfaces in the cells. It is, however, possible to explain most of the results on the alternative hypothesis that the drugs dissolve in and alter the cell lipines. The manner in which narcotics inhibit the action of certain purified enzymes suggests, however, that these drugs act in a similar manner on enzymes *in vitro* and *in vivo*. It should be possible by quantitative comparison of the action of narcotics on enzymes in a purified, lipine-free, condition and on the same enzymes *in vivo* to determine whether certain actions of narcotics are dependent on the presence of lipine.

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⁷ Robertson, Jean, and Clark, A. J., *Biochem. J.*, 1933, 27, 83.

CONTRIBUTIONS TO THE THEORY OF NARCOSIS.

BY KURT H. MEYER.

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Any attempt to elucidate the mechanism of narcosis must take account of two well-known facts: firstly, that the same effect is produced by substances belonging to quite different classes of compounds, with a relatively high chemical inactivity as their only common characteristic; and, secondly, that many narcotics leave the body again completely unchanged, without having, on their part, effected any permanent change in it. This leads to the conclusion, first drawn by H. Meyer and Overton, that the action of narcotics depends on the formation of very loose compounds with certain cell constituents; in the opinion of both these workers these constituents were fat-like substances, the "lipoids."

A later view, maintained by Traube, Loewe, Warburg and others, regards "cell interfaces" as being in general responsible for the adsorption of the narcotic; narcosis would then be the result of adsorption at cell boundary surfaces.

It is possible to decide between these two views experimentally. The present paper describes some work¹ which was carried out with this object and which, furthermore, took into consideration the question whether other cell constituents, *e.g.*, albumens, nucleoproteids, etc., did not also form labile compounds with narcotics.

For every kind of animal or, to be more general, of cell, there exists a certain minimum concentration of the narcotic which must be attained in the surrounding medium, whether air, or water, if narcosis is to be induced and maintained. In the case of water animals this limiting concentration can, with a volatile narcotic, be determined for both the water and the air phase; the concentration found in the water will then equal that in the air multiplied by the absorption coefficient of the vapour of the narcotic in water. A simple physical relationship therefore exists between the two concentrations.

The experimental method employed was to determine the limiting concentration for a number of narcotics as different from one another as possible. It may be assumed that at this concentration a certain partition equilibrium will exist between the organism and the surrounding medium (air or water), and that the concentration which will, in accordance with this partition law, be reached in the cell component on which narcosis depends is then just sufficient for narcosis. The problem is to discover the nature of this essential cell component.

There is hardly any other possibility than to take the limiting concentration and to determine, purely physically, the corresponding concentrations set up in various places: at the boundary surfaces, in the albumens, in the fats (triglycerides) and, finally, in the higher alcohols of the fatty series of the cholesterin type. Oleic alcohol was chosen as the model for substances of the latter class, it being the most closely related of all the readily available substances which might be considered for the purpose.

¹ *Bioch. Z.*, 1935, **277**, 29; 1935, **282**, 444, 447.

Table I. gives for various *gaseous* narcotics the concentrations required to produce narcosis in mice. Further columns give the molar concentrations in albumen, olive oil and oleic alcohol corresponding to equilibrium with this gaseous concentration. The last column indicates whether or not the narcotic is a surface- or interface-active substance.

Table II. shows the concentrations of *water-soluble* narcotics sufficient to cause narcosis in tadpoles and then, as before, gives the corresponding equilibrium concentrations in the various substances.

TABLES I. AND II.

	Concentration in Air Effective for Mice (in vol. per cent.).	Corresponding Equilibrium Concentration in mol./litre in			
		Albumen.	Olive Oil.	Oleic Alcohol.	Surface Activity.
Methane	370	—	0.08	—	o
Nitrous oxide	100	—	0.06	0.06	o
Acetylene	65	—	0.05	—	o
Ethyl chloride	5	0.016	0.07	0.07	o
Ether	3.4	0.06	0.09	0.09	++
Methylal	2.8	0.11	0.08	0.08	++
Carbon disulphide	1.1	—	0.07	—	o
Carbon tetrachloride	0.6	0.003	0.07	0.07	o
Chloroform	0.5	0.005	0.09	0.07	o

	Concentration in Water Effective for Tadpoles (in mol./litre).				
Ethyl alcohol	0.33	—	0.012	0.033	+
Propyl alcohol	0.11	—	0.014	0.038	++
Butyl alcohol	0.03	—	0.02	0.02	+++
Valeramide	0.07	—	0.004	0.021	++
Antipyrin	0.07	—	—	0.021	+
Pyramidone	0.03	—	—	0.039	+
Ether	0.024	—	0.05	0.05	++
Benzamide	0.013	—	0.003	0.033	++
Salicylamide	0.0033	—	0.01	0.021	+
Luminal	0.008	—	—	0.048	+
o-Nitraniline	0.0025	—	—	0.035	+
Carbon disulphide	0.0005	—	0.03	0.03	o
Chloroform	0.00008	—	0.03	0.026	o
Thymol	0.000047	—	0.033	0.045	+

In the first place it will be recognised that there is no kind of correspondence between effectiveness as a narcotic and surface activity; any theory which is based on a connection between these two is accordingly not in agreement with the facts.

On the other hand the following regularity will be observed: the concentration in oleic alcohol as set up in equilibrium with the effective concentration in the medium (air or water) is always constant, or nearly so. The deduction seems inevitable that such a constant concentration is set up also in the body lipoids, *i.e.* in the higher alcohols of the organism, and, further, that great biological significance must be attached to this rule. The experimental observation may be formulated as follows:—

Narcosis commences when any chemically indifferent substance has attained a certain molar concentration in the lipoids of the cell (or, to be

more precise, in the lipoidic alcohols of the cell substance). This concentration depends on the nature of the animal or cell, but is independent of the narcotic.

The above statement seems to me to reproduce best the true nature of the Meyer-Overton lipid theory: it is not really a theory which explains the mechanism of narcosis but rather the expression of an experimentally observed regularity, a rule of which every theory must take account.

Of course this regularity only applies to narcosis caused by the so-called "indifferent" substances and not to the narcotic effect of salts (*e.g.*, magnesium ions) or of substances with a purely specific action, amongst which are certain alkaloids.

This rule has nothing to do with the problem of membranes, at least not for the present. It can merely be stated that cell components composed of substances of the physico-chemical character of the higher alcohols are essential for the normal functioning of the irritability of the cell and that charging these constituents with a certain definite concentration of any indifferent substance interferes with their function, so that the normal irritability (or possibly only, the power of transmitting excitation) is inhibited.

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GENERAL DISCUSSION.*

Professor A. J. Clark (*Edinburgh*), in presenting his communication, pointed out that much of the evidence obtained from the study of narcotics was ambiguous, in that it would accord with more than one physico-chemical theory. The conception that narcotics acted by covering the cell surface with an inert layer was unsatisfactory because although narcotics interfered with the action of some drugs, *e.g.*, cyanides, on cells, yet they did not interfere with the action of other drugs such as acetylcholine. The latter drug was, however, believed to act on the cell surface.

As regards the nature of the cell surface the results obtained from the study of acetylcholine were very difficult to explain except on the assumption that it reacted with specific receptors on the cell surface. Specific receptors of this type seemed most likely to be attached to protein molecules and hence Professor Rideal's hypothesis of a surface composed of a lipo-protein mosaic agreed best with the evidence provided by quantitative pharmacology.

Dr. N. K. Adam (*London*) said: Is it possible that the narcotic acts by dissolving in, and swelling, a lipoid or lipophilic foundation immediately below the active patch, thus altering the particular spacing of the active patch built on this foundation, and destroying its specific adsorptive or activating powers?

Professor Ancel Keys (*Rochester, Minn.*) said: The remarkable gradations in narcotic power found in homologous series have their counterpart in other series of pharmacological agents such as vasodilators, local anaesthetics, etc. Emphasis on these questions, however, tends to obscure the fundamental question: What do *all* narcotics have in common which enables them to exert narcotic action? I should like to ask, as others have for many years, what is the common feature in the alcohols and similar fat solvents, and such diverse substances as carbon dioxide and magnesium salts? Are we to assume with Meyer that CO₂ and Mg⁺⁺ are also "chemically indifferent substances"? Or are we to follow Clark's in-

* On 2 preceding papers.

clination and believe that CO_2 and Mg^{++} "are adsorbed on the surfaces of cells"? I should rather emphasise the fundamental fact that narcotised cells are no longer able to show or transmit irritable responses and that this is a metabolic peculiarity which may or may not, from present knowledge, have its primary origin in an alteration in the cell surface. Another important point is that, in *narcotic* doses, true narcotics do not seriously interfere with the total resting metabolism of the cell. Attempts to make comparisons with, for example, KCN, are obviously misleading and inappropriate for this reason.

Professor H. Freundlich (*London*) said: The surface activity given by Professor Meyer in the last column of Tables I. and II. refers, as far as I can see, to the lowering of surface tension (towards air) of the aqueous solutions of the organic substances mentioned. I rather doubt whether such values are really suitable for testing the adsorption theory of narcosis. For should narcosis actually be caused by adsorption, as I do not wish to imply, one would be dealing probably with an adsorption on a solid or semi-solid lipid surface, not with one towards air. There may be considerable differences between the adsorption on interfaces between aqueous solutions and liquids or solids and that on the surfaces towards air; aromatic substances (such as thymol), for instance, are known to be strongly adsorbable on many solid surfaces but not on the surface: aqueous solution/air. In order to refute the adsorption theory, it would be more conclusive to show that the adsorption of these organic substances on a suitable solid agrees less with their action in narcosis, than does the equilibrium concentration of their distribution between another medium (air or water) and oleic alcohol.

Professor A. J. Clark (*Edinburgh*) said: Regarding the interesting parallel shown in Table II., caution is necessary regarding values obtained by biological measures. The activities of ethyl alcohol, ethyl ether, luminal and chloroform as measured by tadpole narcosis are in the ratio 1:13:40:4000. Experiments on the frog's isolated heart indicate quite different ratios for the same drugs, namely, 1:8:500:300. Quantitative pharmacological data suffer from two disadvantages, firstly, it is very difficult to obtain a reliable measure of drug activity and secondly, different systems are likely to show different results.

Dr. M. Jowett (*Cardiff*) (*communicated*): Experiments which have been made recently by Dr. Quastel and myself,¹ on the effects of narcotics on oxidations in brain slices, are of some interest for the theory of narcotic action.

It has been found that oxidations differ very greatly in their sensitivity to the inhibitory action of narcotics. The oxidation of glucose or sodium lactate, for instance, is inhibited greatly by concentrations of narcotics which do not affect the oxidation of sodium succinate or α -glycerophosphate, as measured by the effects on oxygen consumption. The inhibition of oxidation of glucose begins to manifest itself at concentrations of narcotics of the same order of magnitude as those which narcotise the living animals. This affords some ground for the belief that narcosis may be due to inhibition of oxidation of glucose in the central nervous system, if it be accepted—and there is much evidence for the view—that the functioning of the nervous system depends on the energy derived from oxidations.

Theories of narcosis have seldom been formulated precisely. While it may be admitted that narcotics act by being adsorbed, a theory of narcosis does not become precise—and therefore susceptible to test—until it is stated on what they are adsorbed, and what the effect of that adsorption is.

If narcotics act by being adsorbed on the surfaces of nerve cells, there are two ways in which the adsorption might inhibit cell oxidations:

(1) The permeability may be lessened, so that the supply of metabolites to cells is restricted or the elimination of waste-products impeded. Such effects are likely to lead to a fairly general inhibition of oxidations,

¹ M. Jowett and J. H. Quastel, *Biochem. J.*, 1937, **31**, 565; and unpublished work.

whereas the inhibitions found in experiments with brain slices depend greatly on the particular oxidation in question. Likewise such a retarded diffusion should lead to a considerable dependence of the inhibition on the thickness of the brain slice. No dependence of the inhibition on the thickness has been found.

(2) The permeability of the cell may be increased, leading to the loss from the cells of some diffusible components of oxidising systems. Such a loss would be, under the experimental conditions used, essentially an irreversible process. It has been found,¹ however, that the action of a number of narcotics on oxidations by brain slices is actually reversible. On removing brain slices to a medium containing no narcotic the inhibition of oxidation disappears. Such a recovery in respiration would not take place if the original inhibition were due to diffusion of part of the oxidising enzyme system from the brain slices.

It is considered that the effects of reversible narcotics on oxidations in brain slices are not due to an effect of narcotics on cell permeability. The view is preferred that narcotics inhibit in a direct manner the functioning of some component or components of intra-cellular oxidising systems. The interesting findings of Meyer and Overton and of Professor Kurt Meyer suggest that adsorption takes place on a surface which has chemical groupings in common with those of the higher aliphatic esters and alcohols.

The information so far available suggests that the oxidising systems most sensitive to narcotics are those in which a co-enzyme plays a part, while the less sensitive oxidising systems are not known to require a co-enzyme. Present knowledge is, however, insufficient to decide whether this is a general difference (or if general, the significant difference) between the narcotic-sensitive and the narcotic-insensitive systems. That narcotics act on the more sensitive oxidising systems in brain by inhibiting (after adsorption on dehydrogenase or co-enzyme) the action of co-enzymes, is at present merely one of several possibilities.

Professor I. Traube (Edinburgh) (*communicated*): An objective judgment on the value of the different theories of narcosis can only be obtained by comparison of the Lipoid theories of Overton, H. H. Meyer and Kurt Meyer, with the theories of surface tension, interfacial tension and adsorption of myself, modified by O. Warburg. I may also mention my own theory and my recent discussion with Kurt Meyer.²

I maintain all I have said in my discussion. I wrote in the summary:

1. *Die Narkotika wandern an die Zellwänden entsprechend ihren Grenzflächenaktivitäten. Massgebend ist das Prinzip von Gibbs, sowohl für moleculardisperse, wie für colloide Teilchen. Oberflächenaktiv dagegen sind nur die moleculardispersen Stoffe.*

2. *In den Zellen werden die Narkotika teils adsorbiert, teils gelöst, namentlich in Lipoiden.*

3. *Sie wirken als negative Katalysatoren hemmend auf die verschiedenartigsten Vorgänge (Oxydationen, Enzymatische, bioelektrische Vorgänge usw.) (Siehe meine Abhandlungen in Pflügers Arch. f. d. ges. Physiol., 1904 bis 1928.)*

4. *Ihre Wirkungsstärke ist proportional den Mengen, welche die gleiche narkotische Wirkung haben. Sie kann auch annähernd gemessen werden durch die hemmenden Wirkungen von enzymatischen Vorgängen, etc.*

I should have added that a quite close relationship exists between the efficiency of a narcotic substance and its ability to dissolve a thixotropic gel, such as the protoplasm.

According to the experiments of Shryver,³ and of myself,⁴ the series of the efficiencies of the most different narcotics on tadpoles are quite the same as the velocities of gelatination of sodium-cholate, gelatin, etc.⁵

¹ J. H. Quastel and A. H. M. Wheatley, *Biochem. J.*, 1934, **28**, 1521.

² *Biochemische Z.*, 1935, **277**, 39; **279**, 166; **282**, 444, and **282**, 447.

³ *Proc. Roy. Soc. B*, 1910, **83**, 96, and 1914, **87**, 366.

⁴ *Pflügers Arch. Physiol.*, 1915, **160**, 503, and 1919, **176**, 75.

⁵ See also Jurisic, *Kolloid Z.*, 1936, **78**, 95.

Surface activity exists only for molecular disperse substances and not for substances which are dissolved in water as colloids (*e.g.*, CHCl_3 , CCl_4 , CS_2 , hydrocarbons, etc.), but all these substances have an interfacial-activity. They are concentrated in the boundary planes according to Gibbs' Principle as Traube and von Behren have proved experimentally,¹ by ultramicroscopic observations, Traube and Berceller showed² that chloroform evaporates so quickly out of the aqueous emulsion that the chloroform emulsion becomes quite clear during the time in which a drop in the Stalagmometer is about to drop.

That the solubility in lipoids is important, I never have denied, but Warburg and I have proved that narcotics form the same series and have the same effects if no lipid substances are present. The rule of Kurt Meyer with regard to the concentration in olive oil and oleic alcohol can be interpreted in another way. It has different exceptions in water concentrations.

I cannot agree with Kurt Meyer if he neglects the importance of surface activity and interfacial activity of the Gibbs' Principle and of adsorption.

Professor Kurt H. Meyer (*Genthod-Geneve*), in reply, said: If it is desired to draw conclusions as to the properties determining narcotic efficacy, by comparing narcotic and physical properties (solubility, adsorption, adsorption by enzymes, etc.), it is not legitimate to do so within the limits of a single homologous series. Within these limits, parallelism between narcotic efficacy and physical properties will always be observed, and for the following reason. The vapour pressure, solubility, partition coefficient, adsorption equilibrium, narcotic threshold concentration and other equilibria of the members of an homologous series can be characterised by constants which differ from one member to the next by a constant factor. This behaviour results from the fact that the entropy and energy terms (together constituting the free energy change in the reaction under consideration) receive a definite additional increment for each $-\text{CH}_2$ group. The internal energies (*e.g.*, heats of solution and evaporation) and entropies of a homologous series form an arithmetical series; equilibrium constants therefore form a geometrical series.

The question whether the same series of narcotics found for mice and tadpoles holds for the case of the narcosis of other animals, isolated organs, or cells, can only be answered from my knowledge of the literature. The rule holds for the indifferent narcotics, with slight variations in individual cases.

The more removed the substance in question is from the "indifferent" narcotics, the greater is the possibility of the narcotic effect being masked by other effects, *e.g.*, antipyretic action, poisoning by labile chlorine or bromine (action of CHCl_3 on the heart, toxicity of CH_2Br), and perhaps also specific action on the sleep-centre (veronal series). The more highly differentiated the organism, the more marked will such effects be.

It certainly is possible to bring about the phenomena of narcosis by the action of substances which are entirely different from the lipid-soluble narcotica. This is the case, *e.g.* for morphine, the action of which is limited to certain kinds of animals; also the magnesium-narcosis may be reckoned to this group.

The action of chloroform on the heart, which has already been mentioned by Professor Clark, must be considered as a result of the lability of the chlorine; in fact, this action has not been observed with other halogenated substances, in which the chlorine is bound by stable valencies.³

In reply to Professor Freundlich (*communicated*): Our surface-activity data concern such interfaces as are present in the living organism: aqueous-lipoid. These data thus are connected with interfaces between liquid phases and non-crystalline, amorphous solid phases liable to swell.

¹ *Z. physik. Chemie*, A, 1928, 138, 99 and 100, and *Kolloid Z.*, 1929, 47, 47.

² *Pflügers Arch. f. d. ges. Physiol.*, 1913, 153, 307.

³ Meyer-Gottlieb, *Exp. Pharmacologie*, 8 Aufl., p. 131; Wittgenstein, *Arch. exp. Pathol. Pharm.*, 1918, 83, 236.

Only this kind of interfaces can be found in the animal cells; interfaces of the kind of the surface of charcoal are entirely absent in the cells. A detailed discussion about this point is contained in my publication with Hemmi.¹

In reply to Professor Traube (*communicated*): The fact that CHCl_3 is dissolved in water in the form of single molecules has been demonstrated by the determination of the molecular weight of the solute by the cryoscopic method. The total absence of interface-activity has been shown with the aid of Professor Traube's drop-weight method.² The connection between molecular structure and surface activity has already been mentioned.³

In a more general way, I should like to add that substances with a very high activity are everywhere present in cells and liquors of the animal tissues. As examples may be taken cholesterine and the phosphatides, as well as all soluble proteins. The interfaces in animal tissue must be considered as saturated with substances of this sort.

The sorption of other substances in these interfacial films is limited by the same conditions, which I mentioned in the discussion of page 1017: only if heat is liberated when the new substance penetrates, it is possible that its concentration in the film increases.

Professor Traube in reply (*communicated*) asserted that CHCl_3 is dissolved in water only, or principally, in the form of colloidal aggregates.

¹ *Biochem. Ztschrift*, 1935, **277**, 48.

² *Ibid.*, **282**, 447.

³ See page 1017.

RADIATIONS, CELL PERMEABILITY AND COLLOIDAL CHANGES.*

By PROFESSOR DR. SERGE TCHAKHOTINE (*Paris*).

Received 5th April, 1937.

A new biological discipline has developed in the last decennium, namely *Experimental Cytology*, which associates analytical experimentation with the idea that the essential laws of life manifest themselves in the ultimate living unit, the cell.

These experimental methods are characterised by careful manipulation of the physical and chemical factors affecting the experiments, the use of a whole arsenal of micro-apparatus for operating upon the microscopical objects before, during and after the experiment,¹ and finally by the elaboration of special methods of micro-surgery. These methods, which I have established during the last twenty-five years or so, involve: (1) Mechanical Micro-manipulation²; (2) Ultra-violet Micro-ray Puncture³; (3) Chemical Micro-dissection.⁴

I shall here describe the photochemical operation, or *Micro-photo-surgery* ⁵† It has recently been possible to obtain with this method the following chief experimental results:

(1) To destroy or injure a *single one* in a complex of embryonic cells, e.g. one of the two blastomeres of a *sea urchin* egg, or one of the cells com-

* Except where otherwise stated, the bibliographical references relate to the author's work.

† The apparatus for ultra-violet micro-ray puncture, built now by C. Zeiss in Jena, was exhibited during the meeting, and experiments with living cells were demonstrated.

¹ *Bull. Soc. franç. Microsc.*, 1935, **4**, 138. ² *Z. wiss. Mikr.*, 1912, **29**, 188.

³ *Biol. Zbl.*, 1912, **32**, 623. ⁴ *Boll. Soc. Ital. Biol. Sperim.*, 1933, **8**, 623.

⁵ (a) "Die Mikrostrahlstichmethode und andere Methoden des zytologischen Mikroexperimentes," *Abderhalden's Handb. d. biol. Arbeitsmeth.*, Abt. V, Tl. 10, 1935, 877; (b) *Revue gén. Sciences*, 31 oct., 15 nov., 1935.

posing a *Spirogyra* filament, etc.⁶ The object of this is the study of the embryonic determination of single cellular elements and other problems of experimental embryology and the mechanics of growth.⁷

(2) To activate a sea urchin egg by ray-puncturing one point of its surface in order to substitute the sperm; the interest of this lies chiefly in the clearing up of the physico-chemical mechanism of fertilisation; cellular division followed by cleavage phenomena.⁸

(3) To injure separately the *cell nucleus* or its elements, so as to ascertain its role in several life-phenomena, e.g. division, heredity, metabolic processes such as respiration, secretion,⁹ etc.

(4) To destroy or injure the *single organites* of the cellular body in *Protozoa* or other unicellular organisms or also in isolated cells of multicellular organisms, with the object of studying their significance in cell physiology and pathology and their physical and chemical properties.¹⁰ For instance, it was possible to touch separately different points of the cell surface,¹¹ cilia,¹² vacuoles,¹³ myonemes,¹⁴ sensible organites such as stigma or eye-spot,¹⁵ etc.

All the enumerated facts indicate the great efficiency of the action of ultra-violet light on the living substratum, just as in light therapy.

The problem of present interest is the *mechanism* of this action. How does radiant energy act on the different constituents of living matter which are responsible for the structure and function of the different mechanisms of which the organism is composed?

We may imagine, firstly, a *photochemical action* on specific photo-sensitive substances in the cytoplasm, such as exist in retina purple or in chlorophyll; very many substances can be decomposed by ultra-violet radiation. Or there may be, primarily, a physical action on *cellular enzymes*, stimulating or inhibiting by light their activity, or giving an unusual bias to their specific dynamics, thereby destroying the normal cell metabolic equilibrium as, for instance, when X-rays or γ -rays exercise an action after a long latent period. When, however, as in our case of micro-photo-surgery, the effect is immediate, some other explanation must be sought.

Further, the rays may modify the *surrounding medium*, in which the object is embedded, and resulting toxic products may affect the object. Another explanation might involve modification of the *colloidal state of the cytoplasm*, with subsequent destruction of its essential structures; such colloidal changes, especially of proteins, by ultra-violet light, are well known. Finally, the primary effect of the radiations on the cell may be an action on the *surface layer* of cytoplasm, on the colloids of the cell boundary, with consequent alteration of the normal cellular permeability and entrance of toxic chemical substances which are normally unable to enter the cell.

To investigate this question, I have devised several experiments. In the first I centrifuged a *sea-urchin* egg, whereby the nucleus is projected to the periphery; by aspirating the cell into a thin glass capillary of diameter

⁶ *Bull. Inst. Océanograph.*, 1921, 401.

⁷ See in W. Schleip, *Die Determination der Primitiventwicklung*, Chapter IV. M, and other places, 1929.

⁸ (a) *Boll. Soc. ital. Biol. Sper.*, 1929, 4; (b) *C.R. Soc. Biol.*, 1935, 119, 1394; 120, 714.

⁹ (a) *C.R. Soc. Biol.*, 1920, 83, 1593; (b) *C.R. Acad. Sci.*, 1936, 202, 778.

¹⁰ *Ann. Protistol.*, 1936, 5.

¹¹ *C.R. Acad. Sci.*, 1935, 200, 2217.

¹² *Bull. Soc. franç. Microsc.*, 1936, 5, 61.

¹³ *C.R. Soc. Biol.*, 1935, 120, 782.

¹⁴ *C.R. Acad. Sci.*, 1936, 202, 1114.

¹⁵ *C.R. Soc. Biol.*, 1936, 121, 1162.

smaller than that of the egg, and then releasing it, it assumes a sausage shape, with the nucleus at one end. It is then introduced into a Lantz capillary tube in a sea-water medium with addition of CaCl_2 in excess, which makes the surface colloids more resistant.⁹ By irradiating the end containing the nucleus there is obtained a selective action on the latter by localising the micro-ray puncture at the middle of the egg-sausage so the cytoplasm alone is affected; and if the opposite end is touched peripherally, even in absence of CaCl_2 , the colloids of the surface layer are modified. Thus I could differentiate the action on the various elements of the cell body, with correspondingly different results.

On irradiating the surface layer of a sea-urchin egg,¹⁶ and then irrigating the egg with a hypertonic solution, at the point which was irradiated, a slight concavity appeared. On using a hypotonic medium, instead, of a concavity, there was a protuberance. By means of ultra-violet micro-ray puncture it is possible, therefore, to obtain a localised change of the cell permeability to water (and to other substances): the irradiation causes an increase of permeability by an alteration of the colloids of the surface layer.

To show the action of localised irradiation of cytoplasm, the micro-ray puncture effect is simultaneously observed ultramicroscopically. After irradiation of a small area of the cytoplasm of *Amoeba verrucosa*,¹⁷ a flocculation of colloids is observed at this point, which is, however, perfectly localised.

Finally, an experiment on cells of a Hemiascomycete *Ascoidea rubescens*,¹⁸ shows the play of several factors on irradiating a cellular element: the ultra-violet radiating factor, the cell permeability, the colloidal change of cytoplasm and the H-ion concentration in the surrounding medium. These cells have a very luminous cytoplasm (in dark field illumination) and the vacuome is in the form of an axial syphon; on irradiation there occurs what I will call the "vacuome reaction": the syphon contracts and forms three or four spherical vacuoles, disposed in the longitudinal axis of the cell. The phenomenon is reversible: after a time the syphonal form of the vacuome is re-established. It is due to a colloidal change of cytoplasm, consisting in a swelling of colloids with corresponding modification of viscosity and interfacial tension between cytoplasm and vacuome. This reaction, however, appears only when the p_H of the surrounding medium (normally about 5) is changed towards the alkaline side; in an acid medium, the vacuome reaction does not appear, but the cytoplasm coagulates and the cell dies. The vacuome reaction is obtained also, without irradiation, when in the medium there are alkaline liposoluble substances, which penetrate easily, e.g. ammonia; coagulation and death occurs also when acid liposoluble substances are present, e.g. acetic acid. On irradiation the cell surface layer becomes permeable, alkali penetrates into the cell and causes there the characteristic colloidal change, which provokes the vacuome reaction; in acid media the H-ions penetrate after irradiation and cause coagulation and death.

This serves as an example of many cellular reactions to external stimuli, where factors such as permeability and colloidal changes are involved. Two main phenomena always occur: firstly, the effect of the external stimulus on the surface layer with modification of its permeability, and secondly, alteration of the colloidal substances constituting the living matter with subsequent modification of the cellular structure, metabolism and energy production.

Increase of the permeability of the surface layer by light is compatible with the idea of a cell-membrane structure. Two theories have been suggested: that generally admitted, is that the cytoplasmic surface is covered with a thin layer of specially differentiated substances, of a lipid character, or a mosaic of alternating lipid and protein particles.

¹⁶ C.R. Soc. Biol., 1921, 84, 464.

¹⁷ C.R. Acad. Sci., 1935, 200, 2036.

¹⁸ S. Tchakhotine and P. Gavaudan, C.R. Soc. Biol., 1936, 121, 952; 121, 1323.

The other point of view, especially suggested by Lapicque,¹⁹ is that no specific membrane exists on the surface of the cell, but that permeability phenomena are governed by imbibition of colloids and by electrical factors, where adsorption and the Donnan equilibrium play an eminent role. The action of stimuli is simply depolarisation of surface charges with subsequent modification of metabolic and other actions of the cytoplasm.

The membrane hypothesis appears to me to be the more suitable as an explanation of the observed phenomena. Firstly, micro-surgery shows the real existence of a thin film on the surface of several kinds of cells; Chambers²⁰ could remove and stretch with micro-needles such a film from the surface of amœbæ and marine eggs. By pushing the end of the micro-needle against the surface of many "naked" cells, the surface at this point can be seen to become first curved inwardly before the needle pierces it. By local irradiation of the surface of the unfertilised egg of *Pholas candida* with my micro-ray puncture,⁸ the surface becomes more permeable at the irradiated point, and loses salts; but the injured surface layer speedily recovers and becomes again semi-permeable, if Ca ions are present in the surrounding medium, e.g. the well-known "surface precipitation reaction"²¹ in the case of marine eggs, crushed in sea-water; close to this point, under the relatively thick and rigid chorion layer, the concentration of salts increases temporarily, and this local hypertonic regime causes a slight localised concavity of the underlying portion of the cytoplasm, which lasts a few seconds, until the diffusion of the salt molecules or ions has restored the normal osmotic pressure at this point, when the concavity disappears. These phenomena can only be explained by the membrane hypothesis.

The latest facts about the spreading of *monomolecular protein and lipid films*, studied by Langmuir, Gorter, Rideal, Devaux and others, supports this view. The very small thickness of these films serves to explain why chemical or photochemical reactions occur here with great rapidity, as, for instance, in the above-mentioned action of ultra-violet micro-ray puncture. It is also known that traces of Ca-ions solidify these films, as is also the case in the ray puncture experiments. Langmuir and Blodgett²² could superpose a lot of monomolecular films (about 100-200) one on the other, so that it is not impossible that the cell membrane is formed of different layers of such films, of different chemical and physical character, especially when we have regard to the changes in its permeability. For the latter, I think, the most likely supposition is based on Clowes' ²³ scheme of emulsion changes. The "mosaic" might be constituted by a film-like emulsion of lipid and water-diluted protein elements. By localised irradiation of a small area of such a film both possibilities are given: the lipid (a lecithin-like compound) may be decomposed photochemically and form an alkaline substance, such as choline, which is water-soluble, and will penetrate the interstices of the "mosaic" and make the layer permeable for salts and water. The local irradiation by means of micro-ray puncture of a sea-urchin egg coloured (red) by Neutral red seems to support this hypothesis: the egg becomes yellow, which proves that an alkaline reaction follows the irradiation.²⁴

¹⁹ L. Lapicque, *Ann. Physiol. et Physico-chimie biol.*, 1925, 1, 85.

²⁰ R. Chambers, *Ann. Physiol. et Physico-chimie biol.*, 1930, 6, 233.

²¹ L. Heilbrunn, *Arch. Zellforschung*, 1927, 9, 246.

²² J. Langmuir and Blodgett, *Kolloid Z.*, 1935, 73, 257.

²³ G. H. A. Clowes, *J. Physic. Chem.*, 1916, 20, 407.

²⁴ *Ann. Instit. Pasteur*, 1921, 35, 321.

Another explanation might be that the protein compound of the "mosaic" film is coagulated by rays; coagulation being connected with dehydration, the pores between the elements become larger and molecules which normally could not pass now enter. Coacervation phenomena, like those described by Bungenberg de Jong²⁵ may also play an important role.

So much by way of explanation of the first phenomenon, which involves the effect of radiation on cells, namely the increase of permeability.

The colloidal changes produced in the cytoplasm itself by the radiation can be explained by an action of photo-electrical character. Spiegel-Adolf,²⁶ Boutaric and others have established that ultra-violet irradiation of protein substances in the sol state by a mercury arc causes their denaturation; after irradiation the coagulated mass cannot be dissolved by sodium hydroxide, whilst the product of thermal coagulation, not denatured, is soluble. This denaturation, although not deep enough to break down the protein molecule, is a consequence of the depolarising action of photons on the electrical charges of the large amphoteric molecule of the protein; its electrical symmetry and equilibrium is altered, whereby agglomerations and flocculation result.

The effects described are specific, in relation to the wave-length of the light used; for instance, I could obtain the parthenogenetic action of ultra-violet micro-ray puncture on sea-urchin eggs only with the wave-lengths of 275 and 280 $m\mu$, but not with the band of 293 $m\mu$; there was the same negative result concerning the local contraction of *Paramecium* with 310 $m\mu$; but it was positive, when I previously kept the *Paramecia* in a solution of eosin, which sensitises the living substance to the rays which normally do not affect it. This phenomenon, which is photodynamical,²⁷ can be used with success in the application of the micro-ray puncture method to the study of several facts of cellular physiology. It has also a physico-chemical basis, as Boutaric²⁸ and collaborators have demonstrated; for instance, the flocculation of colloids by electrolytes is accelerated in an illuminated fluorescent medium.

Summary.

1. By means of the ultra-violet micro-ray puncture method, an example of micro-photo-surgery, it is possible to study localised effects of radiant energy on different mechanisms, parts and constituents of the living unit, the cell.

2. In the action of radiations on living matter, it is necessary to distinguish, firstly, the modification of permeability of the surface layer of the cell, which is generally increased by light; secondly, the action of light on the colloidal state of the proteins and other complex substances in the cytoplasm, which can change under the action of radiations and especially coagulate.

3. The changes of permeability are based on the disaggregating action of light on the thin surface films which form the cell-membrane.

4. The actions are specific: they are obtained mostly with the rays of $\lambda = 280 m\mu$, but not, for instance, with 293 $m\mu$ or 310 $m\mu$.

5. It is possible to obtain certain effects by means of micro-ray puncture also with other rays, but only when the object is sensitised with photodynamic substances.

²⁵ H. Bungenberg de Jong, *Protoplasma*, 1932, 15, 110.

²⁶ M. Spiegel-Adolf, *Klin. Woch.*, 1928, 2, 561.

²⁷ H. Tappeiner, *Biochem. Z.*, 1908, 12, 290.

²⁸ A. Boutaric, *Arch. Physique Biol.*, 1935, 12, 227.

PART II.—ARTIFICIAL MEMBRANES.

INTRODUCTORY PAPER:

ARTIFICIAL MEMBRANES: THEIR STRUCTURE AND PERMEABILITY.

BY KURT H. MEYER.

(Received in German, 17th March, 1937.)

The invitation of the Society to give an introductory talk at the meeting devoted to synthetic membranes, was an honour and a great pleasure to me. I accepted this invitation all the more readily, because I regard it as one of the most important tasks of chemistry to supply the biologist with experimental and theoretical material on the basis of which he can continue the investigation of living systems.

If work on the border-line between chemistry, physical chemistry and biology is to be fruitful, it is necessary for workers in these fields to exchange ideas; and those present at this meeting should be grateful to the committee, not only for the opportunity of hearing workers in other branches, but also for the possibility of biologists and chemists establishing contact and getting to know each other personally.

Problems of membrane permeability have occupied biologists for many years; their part in living processes is so important, that, not unnaturally, the workers in this field have been mainly biologists, first place among whom must be given to Traube, to whom we owe the concept of the semi-permeable membrane, and to Pfeffer, who used such membranes for the study of osmotic pressure. It is significant that these workers did not confine their study to natural membranes, but paid special attention to artificial membranes. The value of experiments with artificial membranes lies in the fact that more is known about their composition than about that of the natural membranes and that the controlled production of uniform specimens is easier. With such materials the general laws, to which biological membranes also will be subject, are more likely to become apparent.

In the study of natural membranes we are faced by the additional complication, that in most cases such membranes are built up of at least two different sorts of elements: parts which are permeable to water, ions and water-soluble substances, and parts which are composed of lipoids and which are permeable to lipoid-soluble substances. It has often been supposed that these two components are arranged to form a sort of mosaic.

The chemist can help the biologist by studying both membranes which consist of lipoids and those which consist of water-permeable substances. Indeed, you may be sure that to-day's meeting will also be a mosaic of work on both these topics, and it will be possible for us to

form, from a consideration of the interrelations of all these results, some conception of the functions of natural membranes.

Thus the properties of lipid membranes will be discussed by Rideal and Schulman, who have developed a special experimental technique for the study of surface films. Protein films, which belong to the water-permeable category, will be considered by Gorter and Mitchell. Such monomolecular films are particularly suitable for the study of reactions between dissolved substances and the molecules of the film. On the other hand, for the study of properties determined by texture and porosity, it is impossible to dispense with studies of thicker, artificial membranes, such as those used by earlier investigators, for instance the precipitation membranes of Traube and Pfeffer.

Traube sought to explain semi-permeability by assuming that the pores between the particles of the precipitate constituting his membrane were large enough for the passage of certain molecules but too small for that of others, *i.e.*, the membrane is capable of acting as a sieve; we shall call this action of the membrane the *sieve effect*. Collander¹ has investigated it thoroughly, and has shown that in the case of certain membranes (*e.g.*, precipitated copper ferrocyanide), it suffices to explain the phenomenon of semi-permeability.

Practical use is made of this sieve effect in dialysis and in ultra-filtration. Some degree of perfection has been attained in the production of the ultrafilters and in the determination of their pore-size. This field has been developed especially by Zsigmondy and his school and still further by Bechhold; the subject will be considered at this meeting by Elford and Manegold. The activation energy of diffusion through membranes will be discussed by Danielli.

Parchment paper is another artificial membrane which has been frequently investigated, *e.g.*, by Girard² and by Michaelis.³ It allows anions to pass less easily than cations, and this selective effect is to a great extent unaffected by the size of the ions; the effect was ascribed rather to the electrical charge of the membrane. Michaelis made similar observations on paraffin wax, wax, mastic and rubber membranes, so that no connection between chemical constitution and charge could be discovered. This question was taken further by the work of Höber and his colleagues,⁴ who showed that membranes could be made permeable to cations by the adsorption of acid dyes, while the adsorption of bases produces membranes permeable to anions. The work of Höber and Matsuo, of Mond, and of Michaelis and Fujita on membranes of amphoteric substances, *e.g.*, gelatine, shows that when the p_H existing in the surrounding liquid corresponds to the isoelectric point of the membrane, then this selectivity with respect to ions disappears. On the alkaline side (so that the acid groups of the membrane dissociate), "negative charging" results, and the membrane becomes selectively permeable to cations, while in an acid liquid it is permeable to anions. These membranes indicate clearly the importance of the ionisation of the membrane itself.

Nitrocellulose membranes have been particularly carefully investigated. Collander and Michaelis and his collaborators have shown that

¹ *Kolloidchem. Beihefte*, 1924, 19, 73.

² *Inst. Int. de Chim. Solvay, Conseil Chim.*, 1928, 3, 259.

³ *Naturw.*, 1926, 14, 33, also *J. Gen. Physiol.*; most recent paper: Willbrandt, *ibid.*, 1935, 18, 933.

⁴ *Naturw.*, 1936, 24, 196; *Physiol. Rev.*, 1936, 16, 52.

they can act as a sieve and that they are also selective with respect to ions. But, since nitrocellulose is usually regarded as an unionised substance, it was sought to explain the very marked cation permeability by the adsorption of anions, which were supposed to give a charge to the membrane. This idea was quite in accord with colloid-chemical thought: without further consideration of the chemical character, or the molecular structure or the chemical properties, the membranes were simply idealised as systems of tubes with electrically charged internal surfaces.

It might here be of interest to mention that a dry nitrocellulose membrane is very similar in its selectivity behaviour to a certain plant membrane, namely apple peel, investigated by Loeb and Beutner, in that it exhibits the curious phenomenon known as the concentration effect; the ionic selectivity is much greater at lower than at higher concentrations.

Oil layers constitute a wholly different class of artificial membranes. Overton, and more recently, Osterhout in particular, have investigated these and regarded them as models for cell membranes.⁵

Donnan⁶ considered the membrane problem from quite another point of view. He raised the question of the equilibria which would be set up when solutions of two electrolytes with one common ion are separated by a membrane which is impermeable to one only of the two other ions concerned. The resulting "Donnan Equilibrium" is too well known to call here for more than a statement of the equation for the simplest case: equilibrium will exist when

$$c^2 = (y + A)y,$$

where c is the final concentration of the binary electrolyte on one side, A the concentration (on the other side) of the ion which cannot pass through, and y the concentration of the electrolyte which has passed over into this second side. The concentration of the diffusing ion on the second side will be $A + y$, while the concentration of the non-diffusing ion will remain A . The present state of the subject of membrane equilibrium will be dealt with by Adair.

Donnan hardly touched the question of how such membranes might be obtained or of how the selectivity of natural membranes might be explained. He used well-known semi-permeable membranes—precipitation membranes, parchment, liquids. The ideas developed by Donnan for ideal membranes are nevertheless, as we shall see, of the greatest importance for the theory of membrane permeability itself.

I will now give a brief account of some work which has been carried out recently in Geneva.⁷ Our attitude to the problem was in some measure influenced by the organic chemical atmosphere prevailing in our laboratory, and this led us to investigate membranes of a simple chemical structure enabling us to pay the required attention to the chemical constitution. On the other hand, we were also influenced by our previous work on high-molecular substances, the results of which we applied to the membrane work. In this connection we are indebted to Sir William Bragg, who has shown us that aromatic rings and chain formulæ are not mere formulæ, but that the molecules really do look like that and the rings have such and such a thickness and such and

⁵ Summarising review: Cremer, *Handbuch d. normalen und pathologischen Physiologie*, VIII., 2nd half, 999 (1928); also Höber, *Naturw.*, 1936, 24, 196; *Physiol. Rev.*, 1936, 16, 52.

⁶ *Z. Elektrochem.*, 1911, 17, 572.

⁷ *Helv. Chim. Acta*, 1936, 19, 649, 665, 948, 987; 1937, 20, 634.

such a diameter, and so on. Mark and I have followed this up in the development of spatial models from the formulæ of substances of high molecular weight, such as silk, cellulose, chitin. The proteins, we regard in many cases as flexible threads with lateral ionisable or hydrophobic groups, which in membranes are united to form a network or woven structure. For the carbohydrate chains of the pectins we have developed a corresponding representation.⁸

Up to the present, membranes have generally been represented diagrammatically as continuous bodies traversed by pores, the walls of which were charged either positively or negatively; these walls were supposed to be capable of adsorbing ions. In place of such a model, we now conceive a network of primary valency chains with both lyophilic and hydrophilic groups in lateral positions; of these groups the ionisable or ionised acid and basic groups must be specially mentioned.

Consider a membrane consisting of an acid high-molecular substance, for instance of pectin chains, of which the carboxyl groups have been neutralised with metallic cations, *e.g.*, potassium ions. The membrane then possesses fixed anions and mobile cations. The cations may therefore be displaced if a supply of others is maintained from one side: the membrane is cation permeable. The concentration of the fixed anions, calculated in gram equivalents per litre of the imbibed liquid, is a quantity characteristic for each membrane which we will call the "selectivity constant," A . If now the membrane be immersed in a salt solution, both ions of the salt will penetrate into it; the equilibria then obtaining may be calculated from the Donnan equation: the actual membrane behaves like a solution bounded by two ideal Donnan membranes through which the fixed ions cannot pass. This part of the theory, together with the resulting quantitative deductions, was developed simultaneously by Teorell⁹ and ourselves.

If a current is passed across the membrane, the transport of the electricity will be divided between the two kinds of mobile ions in accordance with the relative numbers of ions passing through the membrane. The ratio, n_C/n_A between the numbers of cations and of anions traversing the membrane, which we will call the ratio of the transport or "traversal" numbers, may be determined by the same methods as those used for the determination of transport numbers in a solution. n_C/n_A depends on the rates of migration of the mobile ions and on their number; as mentioned above, the latter is dependent on the concentration of the ions in the surrounding liquid. We then obtain

$$\frac{n_C}{n_A} = \frac{U_C \cdot (y + A)}{U_A \cdot y} = \frac{U_C}{U_A} \cdot \frac{\sqrt{4c^2 + A^2} + A}{\sqrt{4c^2 + A^2} - A} = \frac{U_C}{U_A} \cdot R,$$

where U_C and U_A are the rates of migration, c the molar concentration of the salt in the surrounding liquid, and A the selectivity constant.

The dependence of the selectivity, *i.e.*, of the quantity n_C/n_A , on the concentration is expressed by the factor R . Its dependence on the ratio c/A is shown by the following table:

c/A	10	1	0.1	0.01	0.001
R	1.1	2.6	101	10,000	1,000,000

⁸ K. H. Meyer, *Bioch. Ztschr.*, 1929, **208**, 1; 1929, **214**, 253; Meyer-Mark, *Aufbau der Hochpolymeren*, Leipzig, 1930. *New Phytologist*, 1931, **30**, 1.

⁹ *Proc. Soc. Exp. Biol. Med.*, 1935, **33**, 282.

If we therefore take a membrane with wide pores such that the concentration of the fixed ions in its aqueous parts is normal ($A = 1$, $c^2/A = c^2$) and surround it with a salt solution the ions of which have equal mobilities, then R will equal the selectivity n_C/n_A . The dependence of n_C/n_A on the external concentration has, as mentioned above, been long known (the "concentration effect"), but so far without having been explained.

Ionic selectivity is not, however, the sole factor governing ionic permeability: in a network the "sieve effect" can also occur, its importance being the greater the finer the mesh of the net; this will in general be the case with membranes which contain little liquid of imbibition. Finally the "solubility" of the ions in the membrane may also play a part. By this we mean that, as a result of the attractive influences of the organic groups of the membrane, some, say organic, ions may attain a greater concentration in the aqueous liquid of imbibition of an organic membrane than in pure water. The complete equation therefore reads

$$\frac{n_C}{n_A} = \frac{U_C}{U_A} \cdot \frac{\sqrt{4c^2 l_C l_A + A^2} + A}{\sqrt{4c^2 l_C l_A + A^2} - A},$$

where U_C/U_A is the ratio of the rates of migration in the membrane under the influence of the sieve effect, and l_C and l_A the solubility coefficients (partition coefficients) of the ions with respect to membrane and water.

Now these two essential properties of the membrane—its sieve action with respect to different ions (as expressed by the quotient U_C/U_A) and its selectivity constant, can be determined by measuring the traversal numbers at different concentrations. The potentiometric method is the best; the potential set up when the membrane separates two solutions of the same salt, but of different concentrations is measured, the absolute concentrations being varied in such a way that their ratio is kept constant. When there is no ionic selectivity the potential is determined only by the quantity U_C/U_A , which is dependent on the absolute concentration; the greater the value of A as compared with the external concentration, the more marked will be the ionic selectivity.

A , the selectivity constant, and U_C/U_A , which includes the expression for the sieve effect, can be quantitatively determined either by calculation or graphically. We will not here reproduce the complicated formulæ required for the calculation, but will merely give a short account of the graphical method.

Curves are constructed plotting as ordinates the potential differences measured between two solutions of the same binary electrolyte, the concentrations (c_1 , c_2) of which are always as 1 : 2, and as abscissæ the quantity $\log \frac{A}{c_1}$. For an electrolyte, the two ions of which have equal mobilities in the membrane (i.e., $U_C/U_A = 1$), a certain curve will then be obtained, while other values of U_C/U_A will result in other curves; a number of such curves are reproduced in Fig. 1.

To determine A and U_C/U_A for an unknown membrane it will then only be necessary to determine several values of E for different absolute values of c_1 , the concentration c_2 being always kept equal to $2c_1$. The observed values of E are then plotted against c_1 (ordinates) using the same co-ordinates as before, and then the experimental curve is displaced sideways (parallel to the abscissa) until it has been successfully brought into co-incidence with one of the curves already drawn; interpolation may be necessary in this procedure. In this way U_C/U_A is determined, the value

depending only on the shape of the curve. The amount of the displacement as read off on the abscissa gives $\log A$, and therefore A . (Fig. 2).

We have prepared a series of membranes and examined their properties.

As predicted by the theory, all membranes consisting of high-molecular substances with attached carboxyl groups were cation permeable. Correspondingly, acid groups could be detected in all cation permeable membranes.

The simplest test involves the use of basic dyes. We emphasise, and this is of great interest to biologists, that all cation permeable membranes

can be stained with basic dyes, *e.g.*, methylene blue or chrysoidine, and all anion permeable ones with eosin or other acid dyes.

The following is a review of the synthetic membranes we have investigated:—

Acetyl cellulose, coagulated with water when moist with glacial acetic acid: $A = 0$, no selectivity, no sieve action. Viscose film (cellophane): very slight cation permeability.

Acid cation permeable membranes: viscose film treated with hypobromite; viscose film stained with a substantive dye containing several sulpho groups: $A = 0.028$; "Glyptal" membrane: $A = 0.19$ Acetylcellulose mixed with "glyptal." Acetylcellulose and polyacrylic acid. All the above membranes were strongly dyed by

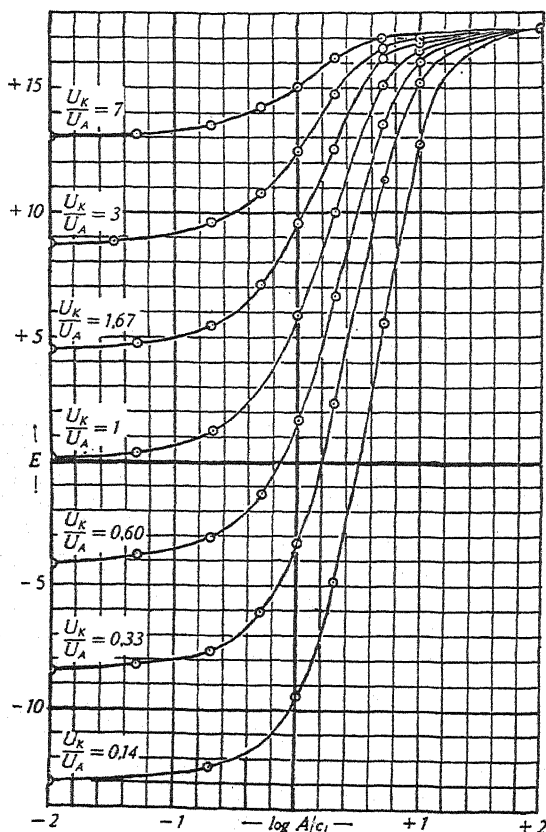


FIG. 1.—Potential-difference E as a function of $\log A/c_1$ for different values of U_K/U_A .

methylene blue.

Acid, cation permeable, fine-meshed membranes exhibiting the sieve effect: Dried nitrocellulose; dry acetylcellulose. The mobility of the Cl ion as compared with the K ion is doubled owing to the sieve effect.

These membranes were analysed by the methods mentioned above.

The acid groups in cellulose consist of carboxyl groups, the detection in nitrocellulose, SO_4H groups must also be considered in addition to the carboxyl groups, and quantitative determination of which have been studied by E. Schmidt.⁹⁰

Special interest attaches to the amphoteric membranes. In these the

⁹⁰ *Ber.*, 1934, 47, 2037; cf. Neale and Stringfellow, *Trans. Far. Soc.*, 1937, 33, 887.

selectivity is a function of the p_H of the surrounding liquid: if this is on the alkaline side of the iso-electric point of the membrane, the latter behaves like a high-molecular acid and becomes cation-permeable; if it is on the acid side, the membrane becomes basic, and is anion-permeable. We have examined and were able to apply the new quantitative relationships to a membrane of the condensation product of phthalic anhydride and triethanolamine; this contains tertiary amino groups together with comparatively few free carboxyl groups; accordingly the membrane is basic, and is anion-permeable in a neutral or acid medium. In an alkaline medium the selectivity is reversed: the carboxyl groups dissociate, the dissociation of the amino-groups is suppressed, and the membrane behaves like a high-molecular acid. The behaviour shown is the same as that of the gelatin membrane studied by Michaelis.

In liquid membranes there are no fixed ions. Accordingly true liquids cannot exhibit the general "cation" or "anion" permeability which may obtain in a membrane with a structure. The number of "mobile" cations is on the contrary equal to that of the "mobile" anions. The ratio of the transport numbers of the two oppositely charged ions of a binary salt will equal the ratio of their rates of migration in the liquid concerned.

The sieve effect will also be absent in a liquid membrane. The phenomena involved in the migration of ions through oil films are therefore less specific than in the case of membranes with a structure.

Nevertheless, the rates of migration in oils may differ considerably from those in water, presumably owing to the addition of the ion to the solvent (solvation). Thus for instance in aniline, not only is the H ion greatly slowed up, as can be explained by the formation of the anilinium ion, but the hydroxyl ion experiences the same effect, and that in a much greater measure; the ions of the alkali metals occupy an intermediate position.

A further factor is the solubility of the ions which in the case of membranes with a definite structure is of scarcely any significance. In the diffusion of a binary salt this makes itself felt only in its effect on the solubility of the salt, which appears to diffuse as a whole. The solubility

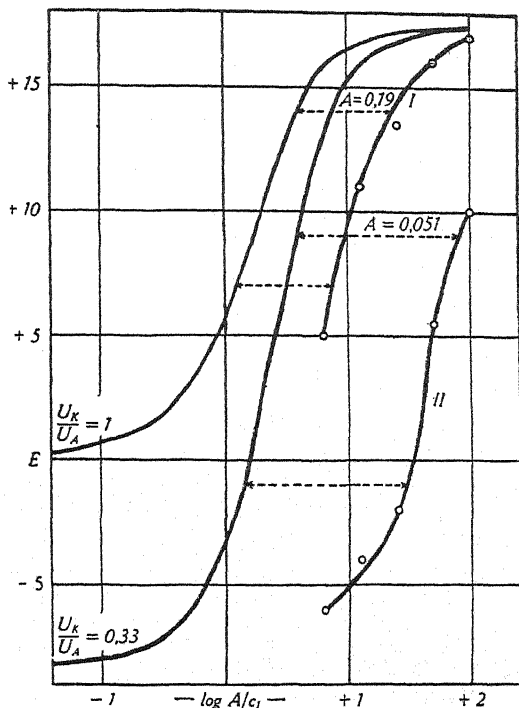


FIG. 2.—Example of graphical determination of U_K/U_A and A . Curve 1: KCl, membrane of acetylcellulose + 70 per cent. polyglycerophthalic acid (membrane markedly acid, no sieve-effect). Curve 2: KCl, membrane of dry acetylcellulose (less acid, marked sieve effect).

of the salt is equal to $\sqrt{l_{A,K}}$. An experimental demonstration of the dependence of the concentration gradient, and therefore of the diffusion rate, on the solubility has been given by Osterhout. When it is a question of the simultaneous diffusion of two similarly charged ions, then their diffusion rates, though also depending on a number of other factors, will be proportional to their solubility. We have ourselves carried out experiments with neutral oils (amyl alcohol) and acid and basic ones (phenol and aniline respectively): the results accord with the above considerations.

We have finally applied the knowledge gained to the study of a few natural animal and vegetable membranes. The bracts of *Iris amcena* proved to be typically cation permeable, with A equal to about 0.02; they exhibited no sieve effect. The membrane therefore contains high molecular acids.

From the potential differences measured by Michaelis and Fujita¹⁰ in the case of apple peel, it can be deduced that this membrane has a selectivity constant, A , of 0.08. The values given by Osterhout and Harris¹¹ for *Nitella* show that the protoplasm is highly selective, while the cell membrane of *Valonia* only exhibits a sieve effect.

By making use of a special artifice, it is also possible to decide whether, in a non-aqueous membrane, the ions migrate through the non-aqueous portion, or pass along fissures filled with water. We found for instance that NH_3 passed through linnoxyn as through an oil-layer, but that ions, e.g., K or $(CH_3)_4N$, certainly migrate along water-filled cracks.

In the course of our study of membranes we have paid special attention to those factors which induce a change in the permeability; primarily, to the fact, first clearly demonstrated by Michaelis, that the selectivity of amphoteric membranes is dependent on the p_H of the surrounding fluid. A change-over in the p_H can thus convert a cation-permeable membrane into a neutral or anion-permeable membrane.

Furthermore, the salt concentration in the surrounding solution can effect either the swelling or the shrinking of the membrane. As imbibition results in the reduction of the concentration of the fixed ions in the water of imbibition, the selectivity will also be reduced, a phenomenon repeatedly observed by us. Similarly the sieve action will also decrease; this is shown very clearly by Osterhout's account for *Valonia*, the "potassium effect" of which can be inhibited by keeping in distilled water.¹²

Of course, the permeability can also be influenced by inducing chemical changes in the membrane itself, e.g. by esterification of the carboxyl groups, or by the attachment of high-molecular acids or bases (staining with dyes); an example of this is the cellophane membrane.

It seems reasonable to assume that many normal permeability changes in the organism are to be ascribed to similar chemical causes. It is known that when work is being done, K ions are liberated from muscle, and it is therefore held that certain membranes in the muscle become permeable to the potassium ion. Now cation permeability is caused in amphoteric membranes by an alkaline reaction, and precisely such a reaction has recently been observed by Muralt during the contraction of muscle.¹³

With the aid of the synthetic membranes described above it is quite easy to obtain several effects required by theory and already observed for natural membranes. Thus, for instance, an anion permeable membrane appears to be permeable to hydrogen ions; actually it is hydroxyl ions which diffuse in exchange for other anions. A selective membrane is also capable of hydrolysing salts, an effect predicted by Donnan. Finally it is possible to construct a galvanic cell which probably represents the mechanism by which current is produced in organisms.

Let a vessel A be separated on one side by a cation permeable membrane from a vessel B, and on the other side by an anion permeable membrane.

¹⁰ *Bioch. Z.*, 1925, 158, 11.

¹² *Ibid.*, 1930, 13, 445.

¹¹ *J. Gen. Physiol.*, 1929, 12, 761.

¹³ *Naturw.*, 1934, 22, 634.

from a vessel C; let B and C be connected by means of non-polarisable electrodes with the electrometer. When the concentration is the same in all three vessels, no current will flow, but if the concentration of ions in A is increased, then B will become positive with respect to C. Using a ratio of ionic concentrations of 1 : 10 we obtained a value of 115 mv.

It must, of course, be recognised, when applying these results to the conditions obtaining in the organism, that matters are as a rule more complicated. These complicated relationships, however, cannot be interpreted unless the laws valid in simpler and more idealised cases are understood.

FACTORS IN MEMBRANE PERMEABILITY.

By ERIC K. RIDEAL.

Received 5th March, 1937.

The effects of adsorption of materials on living membranes appear to be divided relatively sharply into three distinct processes. In the first place adsorption can occur without penetration, secondly penetration can take place with the result that the permeability of the membrane is altered without producing other specific effects and finally both adsorption and probably absorption can take place resulting in the production of one specific effect such as the elimination of a distinct enzyme mechanism.

It is well known that the ionic permeability of membranes can be regarded as being governed by the ionic concentration and mobility inside the membrane, and that these in turn are controlled both by the Donnan membrane equilibrium product and by the volume of liquid containing electrolyte within the membrane. Any alteration in either of these factors, *i.e.*, alteration in the number of ionised groups attached to the membrane or an alteration in what may be termed the free volume of the membrane should alter the membrane potential.

In the past attention has been chiefly confined to consideration of the effects of change in the Donnan distribution caused by increasing or decreasing the number of non-diffusible ionised groups, but it seems probable that the second factor is at least as important as the former and probably provides a clue to the marked effects of various non-electrolytes on membrane potential and membrane permeability. Since natural membranes are composite structures it appeared possible that some progress might be made in our understanding of these reactions by investigating the properties of the simpler constituents spread in the form of monolayers on various substrates and attempting to build up synthetic composite monolayers possessing properties akin to those of the natural membranes. For the last few years Dr. Schulman and I have been attempting to develop this method of approach and already a certain number of interesting facts have come to light. Whilst Dr. Schulman will give a more detailed account of some of the aspects of the work I would like to draw attention to a few of the results which appear to me at least to have definite implications in the consideration of living membranes. In the first place uniform monolayers of proteins may be prepared,¹ and under suitable compressions cross linkage both

¹ Hughes, Gorter, Grendel, Mitchell.

by means of the keto imido groups (which are likewise included in enzyme hydrolysis of peptides) on the main polypeptide chains as well as salt linkage on the side chains may be effected resulting in a gel-like structure. These gel-like structures are readily broken down by the injection of mere traces of fatty acid in the substrate. Certain interesting features are to be noted about the salt linkage and the mechanism of the breaking down of the gel by fatty acids which we shall have occasion to mention.

It is possible to form bridges from one polypeptide chain to another not only by means of the keto imido groups in the chains and salt linkage across the side chains, but by the addition of extraneous material. Some of these extraneous molecules appear to control the resistance to dispersion by fatty acids, rigidity, and thus in three dimensions the extensibility and free volume of protein gels to a very marked extent. For example it is possible to link up a number of polypeptide chains by attachment (presumably through the keto imido linkage) by injection into the substrate of macromolecules containing suitable reactive groups in each unit of the polymer. Two good examples of such macromolecular linkages are to be found in the tannins in which the hydroxyls on the digallyl groups are presumably the linking agents (as in their anti-oxidative action on fat rancidity) and also the macromolecules of silicic

acids $(\text{OH})_2(\text{OH})_2$
 $\begin{array}{c} \parallel \quad \parallel \\ \text{—Si—O—Si—} \end{array}$ effect a similar series of linkages.

Interaction in this manner is even observed with smaller molecules containing two reactive groups, *e.g.*, dyes like Janus green or digallic acid.

We must thus emphasise the reactivity of relatively large molecules possessing a number of reactive groups.

Examination of the properties of films of cholesterol has again provided us with some significant observations. It is found for example that fatty acids injected into the substrate readily penetrate films of cholesterol and form a mixed film in which the molecular ratio is one to one. The phenomenon of penetration of which this is a typical case has led to the study of a number of such systems. Thus mixed films are more stable than films of either component. Composite films of cholesterol and protein likewise possess this feature, provided that the ratio of cholesterol to protein is not too high. The strength of natural membranes may thus be partly attributable to their lipid content.

The great strength of these mixed films, the fact that the molecular ratio for simple molecules when formed by injection of one constituent beneath a film of the other was frequently one to one. (Indeed in the case of the interaction of fatty acids injected under a protein gel it would appear that approximately each peptide unit in the polypeptide chain is associated with one molecule of fatty acid, and in this case penetration appears to be associated with the breaking of the surface bonding), and finally that the formation of mixed films and their stability seemed highly specific led to an extended series of investigations on these systems. We have come to the conclusion that in order to penetrate a monolayer and form a stable mixed film, there has to be in the first instance an interaction between the polar head group presented by the film to the substrate and the polar head group of the penetrating agent, this interaction in some cases necessitating the breaking of a pre-formed link in the film-forming material. Secondly both film forming material by necessity and penetrating agent by choice have to possess relatively large non-polar

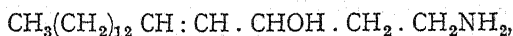
portions. The stability of the resulting binary complex is thus attributable to two separate interactions, van der Waals' interaction between the non-polar portions of the molecule and interaction between the head groups. It has frequently been suggested that salt linkages (*e.g.*, $-\text{COOH} + \text{NH}_2-$) form the chief interlinkage systems and reactive groups in natural membranes but as we have seen keto imido interlinkage as well as Van der Waals' adhesion can occur. Without adopting extreme views ² these keto imido bonds may be regarded as co-ordinated hydrogen linkages, ³ *e.g.*, $-\text{CO} \cdot \text{H} \cdot \text{N}-$. It is an interesting observation that all the polar head group interactions which we have examined hitherto can be expressed in terms of a hydrogen link. We must, however, observe that Katz obtained adsorption reactions with compounds such

as $\text{SC} \begin{array}{l} \text{R} \\ \diagup \\ \text{R} \end{array}$ and $\text{ICH}_2 \text{COOH}$. The stability of the head group interaction

of the resulting complex varies, however, within wide limits and it would appear preferable to regard these interactions as chelate, usually between a proton donator and a proton acceptor, the stability of the complex being dependent on the donative and acceptive powers of the two groups, which in turn are dependent upon the structure of the rest of the molecule. Thus the polarisability of the molecule or the portion of the molecule attached to an OH group (*e.g.*, a conjugated chain system) in the sense employed by Lennard-Jones in considering the molecular orbitals of hydrocarbons is an important factor in this connection. The hydrogen atom may be regarded as providing a convenient locus for interaction of the electron systems of both groups.

Many of these mixed films withstand pressures of 60 dynes/cm. without breaking up. If we consider this breaking process as a dissociation of the complex we may assess the free energy change in formation of such complexes as lying between 1-10 kg. cal. per gm. mol. A few of these complexes, *e.g.*, that resulting from the interaction between a long chain sulphonic acid and cholesterol or the formation of acid soap are sufficiently stable to be detectable in bulk phase but the majority of them are characteristic of interphases alone.

It is possible to combine a number of highly reactive groups in one complex molecule, and we note with interest the high activity in these surface phenomena of both the naturally occurring phospholipins and galactolipins. Sphingomyelin and its base sphingosine,



have been found to be especially reactive.

We have not examined lecithin itself in detail but the specific activity of an ester group has already been established as a proton accepting system, suggestive in connection with the antagonistic action of lecithin and cholesterol (Theorell and Widstein) in blood cell hæmolysis. The well-known difficulties which arise in ensuring freedom from fatty acids in lecithin suggest that observations on systems containing lecithin must be taken with reserves.

Another phenomenon is to be observed in these film reactions, *viz.*, a carrier action. It is found for example that both aliphatic long chain acids as well as long chain alcohols can form complexes with polypeptide chains but whereas the acids are readily soluble in the form of the ions

² *E.g.*, Wrinch,

³ Sidgwick.

the transport of the alcohol is rendered difficult by reason of its insolubility, the complex between acid and alcohol is however readily dispersed and the alcohol can be carried in this manner. It is subsequently released for interaction as the acid and alcohol can combine with different portions of the protein (a proton donating and proton accepting group respectively).

Another similar transportation complex is to be found in the case of the interaction of glycocholate or taurocholate ions with the long chain fatty acids and the passage of these latter through the intestinal wall probably takes place by means of this mechanism.⁴

The secondary alcoholic group of cholesterol—one of the strongest proton donating groups examined—reacts readily with the carboxyl or sulphonic ion with the result that films of cholesterol are readily penetrated by fatty acids. We may note the interesting parallelism between this film penetration process and the bacteriolysis of some bacteria by saponin after sensitisation by cholesterol.

If we regard natural membranes as essentially a protein network in which other substances may be distributed in a regular or haphazard manner we note that many of these foreign substances can participate functionally in the membrane structure, acting as bonding or disruptive spots in the bulk phase. Substances reacting with the membrane may either form bonds or disperse the bonds of the interprotein links or may act specifically (and even quantitatively thus exhibiting "saturation" phenomena) on the foreign material present in the membrane and in turn affect their function, as bonding or dispersing centres. If they react on specific enzyme groups, *e.g.* cytochrome, a metabolic reaction ceases, but these interactions may also affect both the number of fixed ions in the gel and thus the Donnan distribution as well as free volume of electrolyte and thus the membrane rigidity, permeability, and potential.

The inhibition of secretion of aniline dyestuffs into isolated frog's liver in Ringer solution by various non-electrolytes such as disaccharides, thiourea as well as amino acids and sodium salts of aliphatic acids observed by Höber and Titagew⁵ might be ascribed to the blocking of specific dyestuff acceptive groups by prior reaction with these substances, examination of the data suggest that proton accepting groups present in the liver but absent in the frog's kidney may play an important part in the secretion of the dyes.

In the same way we may introduce into a gel structure which is relatively lyophilic a number of lyophobic groups either chains or rings provided that we attach to these non-polar portions suitably reactive polar heads, in this way the relative permeability of the membrane to water and to hydrocarbons may be affected.⁶

The bonding of a fatty acid to a protein is weaker than that of the secondary alcohol of cholesterol in consequence the permeability of the membrane to fatty acid is much greater than for cholesterol, the movement of substances through the gel being regarded as a species of activated migration.

We may conclude that substances which exert narcotic action must

⁴ Verzar and Kutky, *Biochem. Z.*, 1929, **205**, 369; **210**, 265; Gardner and Gainsborough, *Quart. J. Med.*, 1930, **23**, 465; Fürth and Scholl, *Biochem. Z.*, 1930, **222**, 430.

⁵ *Arch. ges. Physiol.*, 1929, **223**, 180.

⁶ Machehoeff, *C.R.*, 1931, **192**, 1413, on water transport to tissue.

be capable first of penetrating the gel system, *i.e.*, should preferably possess an active group if they enter through either the protein network or the lipoid portion (such an active group, *e.g.*, the NH_2 or secondary alcohol or $-\text{COOH}$ is essential for the protein penetration) they should also possess a sufficiently large hydrophobic portion so that the complex formed with one of the constituents (enzyme or co-enzyme) should possess sufficient stability. Since there appears to be a definite amount of enzyme system embedded in unit volume of the membrane substances which are strongly and specifically adsorbed will exert their narcotic action when a definite number of molecules have penetrated unit volume of the membrane.

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GENERAL DISCUSSION.*

Professor E. Manegold (*Dresden*) said: The Meyer-Teorell quantitative theory of permeability can be very well applied (so far as concerns the sieve-effect) to glass membranes which were considered by Michaelis in connection with the potential of the glass electrode. Brittle glass contains a fixed $-\text{O}-\text{Si}-\text{O}-$ lattice of which the negative charges can be compensated by immobile surplus cations and mobile alkali ions.

A pure sodium glass from about 400° to 500° C. represents a 100 per cent. Na^+ ion conductor, *i.e.*, under the influence of a potential drop only the Na^+ ions can pass the negative charges of the lattice; if Na^+ ions are electrolysed across such a glass from a melt of NaNO_3 or from sodium amalgam the glass remains unaltered. If, however, instead of Na^+ ions larger cations are passed such as K^+ ions from a melt of $\text{KNO}_3 + \text{KNO}_2$ or from potassium amalgam, the substitution of Na^+ ions by K^+ ions shows itself by a very large increase of the ohmic resistance in the anodic layer of the glass. Moreover, the mechanical pressure between the unaltered Na-glass and the K-glass of the anodic layer becomes so large that frequently the anodic layers breaks off as a sharply defined layer from the unaltered glass.

Cæsium ions would seem, from space considerations, to be by no means adapted to replace Na^+ ions electrolytically. If we separate two CsNO_3 , NaNO_3 melts of different CsNO_3 content through a glass membrane it is only the sodium ions which can pass through the membrane.

This type of permeation is, however, quite different from that which takes place through a coarse capillary system and different from diffusion since, within the glass membrane, no concentration gradient of Na^+ ions is set up, so far as can be seen, from changes in the concentration at the two limiting surfaces. The transit appears—formally considered—to be quite like that of an incompressible fluid through a tube at the two ends of which a constant pressure difference is maintained.

Lottermoser has observed that the positive charge on particles of an Al_2O_3 or AgI sol can be shifted by simple dilution. This shift can be related with the Meyer-Teorell theory if we assume for the sol particles, a sponge-like structure, the spacing of which is determined by the equilibrium between the repulsive electrical forces of the lattice charges and the cohesion forces between the lattice elements.†

* On 2 preceding papers.

† According to Waitz the attractive force which the lattice charges exert on the lattice is expressed by $Z = \frac{\epsilon}{8\pi} \left(\frac{\Psi}{R} \right)^2$ dynes/cm.² where Ψ is the potential of the particles in e.s.u., R the radius of the particles in cm. and ϵ the dielectric constant.

In the pores of the spongy—coherent secondary—particles there are present Gegenions of the positively charged lattice and foreign electrolyte molecules. If now the sol is diluted a concentration gradient of the electrolyte molecules is set up and the ions have a tendency to wander out from the particles; if the anion is slower than the cation (having regard to its dimensions and the positive charge of the lattice) a dialysis potential, opposed to the positive charge of the lattice is set up. This suggestive potential drop leads to a weakening of the electrostatic forces or an increase of the cohesion force, as a consequence of which the particle contracts and blocks the path of the anions still more strongly. In this way a slight discharge of a positively charged particle can be explained.

Dr. P. Grabar (*Paris*) said: It seemed highly interesting to be able to utilise membranes prepared from absolutely neutral substances, and we have therefore sought, together with Mme. A. Dobry, to prepare membranes from polystyrols. Our technique does not, as yet, give uniform results, but we can already make such membranes of a sufficient strength to be handled with ease in experiments of electro-osmosis.

Dr. W. Wilbrandt (*Bern*) said: I should like to mention an observation I made when working on the potentials of dried collodion membranes in Professor Michaelis' laboratory,¹ which finds now an explanation by the theory advanced by Professor K. H. Meyer and Dr. Teorell. Studying the properties of membranes impregnated with basic dyestuffs, I found membranes with an asymmetry potential of rather amazing magnitude. The concentration effects, measured for both sides of such a membrane separately, turned out to be different, and the more so, the higher the asymmetry potential. By combining an ordinary cation-permeable dried collodion membrane with an almost exclusively anion-permeable impregnated membrane (sticking them together) it was possible to produce such asymmetric membranes at will. They showed asymmetry potentials up to 450 mv. This extraordinary magnitude of the potential difference was hard to explain along the lines of Michaelis' theory of membrane potentials, in which diffusion potentials were involved only. If, however, there are at the surfaces of the membrane high potential jumps, which cancel out in a symmetrical membrane, they may add up in an asymmetric membrane, so that a very high total potential difference would be expected. In biological systems such asymmetries may play an important rôle.

Dr. T. Teorell (*Uppsala*) said, referring to Professor Meyers' paper 2: In regard to the theory of potentials in charged membranes as worked out by myself and Meyer and Sievers² some weaknesses have to be considered: (1) A steady state must be attained. (2) The diffusion across the membrane should be slow so as to secure complete interfacial Donnan distributions. This means either low ionic mobilities within the membrane, or that the membrane is comparatively thick. The validity of this point may become doubtful when considering extremely thin membranes. (3) The ions of the water, H and OH, are neglected, also the "Gegen" ions to the immobile membrane ion are disregarded, they are, however, exchanged during the early stages of the diffusion against bulk ions.

The formula presented³ dealt only with the case of one 1 — 1 valent electrolyte employed in two different concentrations on the two sides of the membrane. A formula for a case of the type KCl/NaCl can be derived from the same principles. The general expression valid for concentrations $KCl \neq NaCl$ is somewhat too bulky to be reproduced here. For the special case that $KCl = NaCl$ it reduces to the following form (for a negative membrane)

$$\text{total membrane P.D.} = 58 \log \frac{(u_K + v_{Cl})r - v_{Cl}X}{(u_{Na} + v_{Cl})r - v_{Cl}X}.$$

¹ *J. Gen. Physiol.*, 1935, 18, 933.

² Cf. remarks on p. 1054.

³ P. 1077.

Here $r = 0.5X + \sqrt{a^2 + 0.25X^2}$, a denotes the salt concentration in the bulks, X the "concentration" of the (negative) membrane and the u and v ion mobilities respectively. This formula, however, does not seem to agree so well with the experimental data available (for instance Michaelis' experiments on "chemical potentials" on dried collodion). One has to remember that the theory operates with highly simplified assumptions.

Mr. J. J. Bikerman (*Manchester*) said: Professor Meyer states: "If the current is passed across the membrane" the ratio n_e/n_a is given by his second equation. Now, if the current is passed across the membrane, the field strength and the ionic mobilities within the membrane are functions of the concentration ⁴ so that the expression is not complete. Fortunately in the experiments reported by Professor Meyer the potentiometric method was used so that there was no current at all and the calculations are not affected.

Professor Meyer in deriving his final formula has assumed ⁵ that both walls of the membrane are effectively in a state of equilibrium with the surrounding solutions, and that the drop of concentration occurs within the membrane only. An important consequence of this hypothesis is that the rôle attributed to mobilities is strongly reduced. I do not know whether this assumption is invariably valid. If the measured membrane potential depends on the thickness of the membrane, Professor Meyer's equation would be applicable to the potential observed in the limiting case of very thick membranes, whilst the formula used by Michaelis would hold for the limiting case of very thin membranes. Does the potential vary with the thickness of the membrane?

Mr. O. Gatty (*Cambridge*) said: It is necessary to remember that oriented dipoles can only produce permanent changes in the electrical potential across an interphase that allows the passage of ions so long as the system is not in thermodynamic equilibrium; it is, of course, possible for oriented monolayers to maintain a potential provided metabolism is going on and for these layers to modify diffusion potentials.

Professor Kurt H. Meyer (*Genthod Geneve*), in reply, said: With regard to the oft-discussed question whether we observe phase-boundary potentials or diffusion-potentials when two electrodes are separated by a solid or liquid intermediary layer, the following may be said. Each such potential may be regarded as a diffusion potential if all pertinent factors such as solubility, Donnan-distribution, etc., are taken into consideration; on the other hand we may consider the potential as consisting of two phase-boundary potentials together with a diffusion-potential in the intermediary layer. Both methods of calculation give the same result.⁶

As to the influence of the thickness of the membrane mentioned by Dr. Teorell: what is measured is the sum of all individual potential-differences from the one electrode to the other; if diffusion takes place during measurement, the real membrane potential will only be observed if the same concentration is maintained at the boundary surface as prevails in the bulk of the solution of the electrolyte. This may be achieved by stirring. In practice we chose a membrane so thick that the rate of diffusion in the solution was high as compared with that in the membrane. The formulæ given in our work only apply to the latter case.

If the membrane is thin, the character of the boundary layer may change as a result of rapid diffusion, so that the relationships are less susceptible of analysis. A thin cellulose-film selectively permeable to cations as a result of staining with a direct dye, shows at first a high potential-difference on placing between two KCl solutions of different concentrations; the difference soon falls to half the original value, but increases on stirring to the initial level.

⁴ J. J. Bikerman, *Z. physikal. Chem. A*, 1933, **163**, 378; *J. physikal. Chem.*, 1935, **39**, 243.

⁵ *Helv. Chim. Acta*, 1936, **19**, 649.

⁶ *Ibid.*, 662.

Whether ions pass through a non-aqueous lipid layer (as Osterhout has supposed in the case of *Valonia*) or through water-filled cracks, may be tested in the following way. A membrane is bounded on one side by KCl, and on the other by an isotonic mixture of KCl with increasing proportions of $(\text{CH}_3)_4\text{Cl}$. On account of its large size the $(\text{CH}_3)_4^+$ moves more slowly than the K^+ in water, and through water-filled pores, but (since it is lipid soluble) much more rapidly than K^+ in non-aqueous layers. If, therefore, the potential measured in the solution containing $(\text{CH}_3)_4^+$ becomes more negative (the positive current flowing from this solution through the membrane into the KCl-solution), we conclude that transport takes place through a non-aqueous layer. If the converse is observed the ions must pass through aqueous regions.

This method, together with the others described by us for the quantitative study of artificial membranes, may be applied with some hope of success to "membranes" in Krogh's sense. If the membrane is the site of chemical reactions, *i.e.*, if it contains a "dynamic machine," the true diffusion-potentials may be masked by such processes.

THE EFFECTIVENESS OF FILTRATION, DIALYSIS, ELECTROLYSIS AND THEIR INTERCOMBINATIONS AS PURIFICATION PROCESSES.

BY ERICH MANEGOLD.

Received in German, 1st March, 1937.

It being desired to purify a hydrosol contaminated with a molecularly disperse constituent (*e.g.* a foreign electrolyte) by means of filtration, dialysis, electrolysis or any desired combination of these three fundamental methods, we ask what is the efficiency of each of the seven possible purification processes; * the magnitude of the effect being expressed in terms of the time (in seconds) required to reduce the concentration of the foreign electrolyte from its initial value to a given final value, a prescribed experimental arrangement and a given membrane being employed.

The essential factors concerned are the hydrosol, the foreign electrolyte, the membrane, and the experimental arrangement.

1. The Hydrosol.

A polydisperse non-electrolyte will be considered, the magnitude of the smallest particles being:

$$2R = 50 \times 10^{-7} \text{ cm.}$$

2. The Foreign Electrolyte.

The uni-univalent foreign electrolyte will be assumed to be completely dissociated, its ions exhibiting no differences in mobility either within or outside the membrane ($u_k = u_a$). Taking its diffusion coefficient and molecular diameter as identical with that of hydrochloric acid:

$$(k^* = 2.54 \times 10^{-5} \text{ cm.}^2/\text{sec. at } 18^\circ \text{ C. } 2R = 0.137 \times 10^{-7} \text{ cm.}),$$

* The seven possible purification processes are: Electro-Filtration-Dialysis, E.F.D.; Electro-Filtration, E.F.; Electro-Dialysis, E.D.; Filtration-Dialysis, F.D.; Filtration, F.; Dialysis, D.; Electrolysis, E.

and taking the diameter of the water molecule as : $2R = 0.113 \times 10^{-7}$ cm. we write the initial and final concentrations of the foreign electrolyte c_e^0 and c_e gr. equiv./cm.³ respectively.

3. The Membrane.

(a) **General Observations.**—Firstly, the capillary system of the selected membrane must be such that the smallest colloid particles cannot pass, only the molecules of the foreign electrolyte or of the water being able to pass. The capillary diameter must accordingly be less than 50 and greater than 0.14×10^{-7} cm.; this range of permissible capillary diameters corresponds to the length of about 450 water molecules. To facilitate the passage of the water and foreign electrolyte molecules, it is obviously desirable to choose a membrane with a capillary diameter lying as closely as possible below the upper limit. Further, the length of the capillaries should be as small as possible, while their number per unit area should be as great as possible.

As a representative measure of the capillary diameter we may take the water transmissivity (*Durchlässigkeit*) (D); for their length we take the thickness (d) and for their number the porosity (*Hohlraumvolumen*) (W) of the membrane. Quite generally, the highest rate of purification will be attained if the membrane selected combines the greatest possible water transmissivity and porosity with the least possible thickness.

The thickness, d , may be measured micrometrically; the porosity can in the simplest case be calculated from the equation

$$W = \frac{G_n - G_t}{F'd} \quad . \quad . \quad . \quad (1)$$

where G_n is the weight in gm. of F' cm.² of the water-saturated membrane and G_t that of the same water-free membrane.

(b) **The Water Transmissivity and the Capillary Width.**—The transmissivity D is fundamental to a quantitative description of the filtration process; it is defined by

$$D = \frac{Q}{Ft(p_e - p_a)} \text{ c.c./cm.}^2 \text{ sec. gm./cm.}^2, \quad . \quad . \quad (2)$$

where Q is the volume in c.c. of the water passing at the experimental temperature through F cm.² of the membrane in t seconds when the difference in pressure is $(p_e - p_a)$ gm./cm.²

Using the Hagen-Poiseuille law, the following equations can be deduced for various arrangements of discrete capillary channels within the membrane substance :

For cylindrical channels (pores) permeating the membrane from one surface to the other but without preferential direction, the radius of the pores is given by

$$r_3 = \sqrt{\frac{24Dd\eta}{W}} \text{ cm.} \quad . \quad . \quad . \quad (3)$$

where η = is the coefficient of viscosity of the water at the experimental temperature (in gm./cm. sec.).

For rectangular channels (slits) analogously arranged, the half-width of the slit is given by

$$\beta_3 = \sqrt{\frac{4.5Dd\eta}{W}} \text{ cm.} \quad . \quad . \quad . \quad (4)$$

$$(r_3 = 2.31\beta_3)$$

The number of pores (N_3) or the slit length (L_3) (as the case may be) per cm.² of membrane is given by

$$N_3 = W/2r_3^2\pi \quad . \quad . \quad . \quad (5)$$

$$L_3 = W\pi/8\beta_3 \text{ cm.} \quad . \quad . \quad . \quad (6)$$

(c) **The Permeability** (*Permeabilität*) (δ^*).—The efficiency of the membrane for dialysis of the foreign electrolyte will be measured by the permeability δ^* in cm./sec.; it is defined by:

$$\delta^* = \frac{S}{Ft(c_e - c_a)} \text{ cm./sec.} \quad (7)$$

where S is the quantity of substance (in gm. equiv.) which, in the stationary state and at the experimental temperature, permeates in t seconds through F cm.² of membrane under a concentration difference of 1 gm. equiv. per c.c.*

Provided that the dialysing molecules are not impeded within the membrane, either electrically or by geometrical causes, the following relationship connects the permeability of a substance through a system of channels oriented as above mentioned and the free diffusion coefficient of that substance:

$$\delta^* = \frac{k^*W}{3d} \text{ (for pores)} \quad (8)$$

$$\delta^* = \frac{k^*W}{1.5d} \text{ (for slits)} \quad (9)^\dagger$$

(d) **The Collodion Membrane** serving as a basis for the subsequent calculations has the following magnitudes: $d = 2.94 \times 10^{-2}$ cm.; $W = 0.932$; $D = 12.2 \times 10^{-7}$ at 18°C. ; $\delta^* = 5.5 \times 10^{-4}$ at 18°C.

The free diffusion coefficient of hydrochloric acid calculated from this value of the δ^* using equation (9) is $k^*_{\text{calc.}} = 2.46 \times 10^{-5}$, and the experimental value is 2.54×10^{-5} cm.²/sec. If an unoriented slit structure be accordingly assumed for the membrane, the half-slit width of the channels is given by equation (4) as $\beta_s = 13.2 \times 10^{-7}$ cm.

With such a capillary width ($2\beta_s = 26.4 \times 10^{-7}$ cm.), we are therefore sufficiently below the permissible upper limit, having a considerable margin of safety.

(e) **The Osmotic or Electro-osmotic Transfer of Water and the Electrical Conductivity of the Membrane** can be neglected, as they are in most cases of a lower order of magnitude. Deviations from neutrality will also not be considered.

4. The Experimental Method.

(a) Other things being equal, the greater the area of membrane for a given volume of hydrosol, the greater will be the rate of purification by any given method. In our experimental arrangement¹ the hydrosol is placed in a cylindrical glass vessel, the open ends of which are covered by the membrane specified above.

The volume of the hydrosol is $v_0 = 100$ c.c. and the total area of membrane F is $= 77$ cm.²

(b) Variations in concentration arising in the hydrosol during the experiments are equalised by continuous stirring, and a vigorous current of pure water is continuously led past the outside surface of the membrane, so that the external concentration of the foreign electrolyte can be taken as zero ($c_a = 0$).

(c) The liquid filtered off during filtration under the pressure difference of $(p_e - p_a)$ gm./cm.² is continuously replaced by an equal volume of water, so that the volume of the hydrosol v_0 is kept constant.

(d) The current strength, i , is also kept constant potentiometrically throughout the experiment.

* The permeability per unit concentration gradient—i.e., δ^*d —will be called the permeation coefficient. Its dimensions are cm.²/sec.

† The quotient $\frac{\delta^*k}{k^*}$ will here be designated the specific permeability. It is of zero dimension.

¹ E. Manegold, *Kolloid. Z.*, 1937, 78, 129.

The Velocity Equations.

(a) The General Differential Equation.

The most general and comprehensive purification method is electro-filtration-dialysis. In the stationary state the drop in foreign electrolyte concentration resulting in the time dt is

$$-dc_e = \frac{i}{v_e^0} \left[\underbrace{\frac{i}{96500}}_{\text{Electrolysis}} + \underbrace{\{\delta^* + D(p_e - p_a)\}}_{\text{Dialysis}} c_e F \right] dt.$$

\uparrow \uparrow \uparrow
 Electrolysis Dialysis Filtration

(b) Electro-filtration-dialysis.

Integration of the above equation gives the general expression for the time (in seconds) required to reduce the concentration of the foreign electrolyte from its initial value, c_e^0 , to c_e , viz.,

$$t_e = \frac{v_e^0}{F\{\delta^* + D(p_e - p_a)\}0.4343} \log \left[\frac{i + c_e^0\{\delta^* + D(p_e - p_a)\}F96500}{i + c_e\{\delta^* + D(p_e - p_a)\}F96500} \right] \quad (10)$$

(c) The Various Special Cases.

The special equations for the other six methods follow directly when the magnitudes i , δ^* or $(p_e - p_a)$ are respectively put equal to zero.

Electro-filtration ($\delta^* = 0$):

$$t_e = \frac{v_e^0}{F \cdot D(p_e - p_a)0.4343} \log \left[\frac{i + c_e^0 D(p_e - p_a)F96500}{i + c_e D(p_e - p_a)F96500} \right] \quad (11)$$

$$\text{Electro-dialysis } ((p_e - p_a) = 0): t_e = \frac{v_e^0}{F\delta^*0.4343} \log \left[\frac{i + c_e^0\delta^*F96500}{i + c_e\delta^*F96500} \right] \quad (12)$$

$$\text{Filtration-dialysis } (i = 0): t_e = \frac{v_e^0}{F\{\delta^* + D(p_e - p_a)\}0.4343} \log \frac{c_e^0}{c_e} \quad (13)$$

$$\text{Filtration } (i = 0 \text{ and } \delta^* = 0): t_e = \frac{v_e^0}{FD(p_e - p_a)0.4343} \log \frac{c_e^0}{c_e} \quad (14)$$

$$\text{Dialysis } (i = 0 \text{ and } (p_e - p_a) = 0): t_e = \frac{v_e^0}{F\delta^*0.4343} \log \frac{c_e^0}{c_e} \quad (15)$$

Finally, Simple electrolysis ($\delta^* = 0$ and $(p_e - p_a) = 0$):

$$t_e = \frac{v_e^0(c_e^0 - c_e)96500}{i} \quad (16)$$

It is therefore only in the case of filtration, dialysis or filtration-dialysis that the time of purification, t_e , is independent of the absolute value of the initial concentration.

Results.

Using now for the experimental variables: $c_e^0 = 10^{-3}$ gm. equiv./c.c., $(p_e - p_a) = 10^3$ gm./cm.² and $i = 1.00$ or 0.10 or 0.01 amp., the final concentration being expressed as a fraction (x) of the initial concentration, so that $c_e = xc_e^0$, the corresponding purification times are readily calculated.

Fig. 1 shows the value of x as a function of t_e , for the seven different purification methods, for the membrane and experimental conditions characterised above. From these curves the time required to reduce the concentration to $\frac{1}{10}$ or $\frac{1}{100}$ (say) of its initial value can be easily obtained. They show very clearly how relatively small is the purification rate due to electrolysis compared with filtration or dialysis. But the contrary obtains at very small electrolyte concentrations because the current strength is maintained constant; if, instead, the potential difference across the electrodes were maintained constant, then, as the electrolyte content

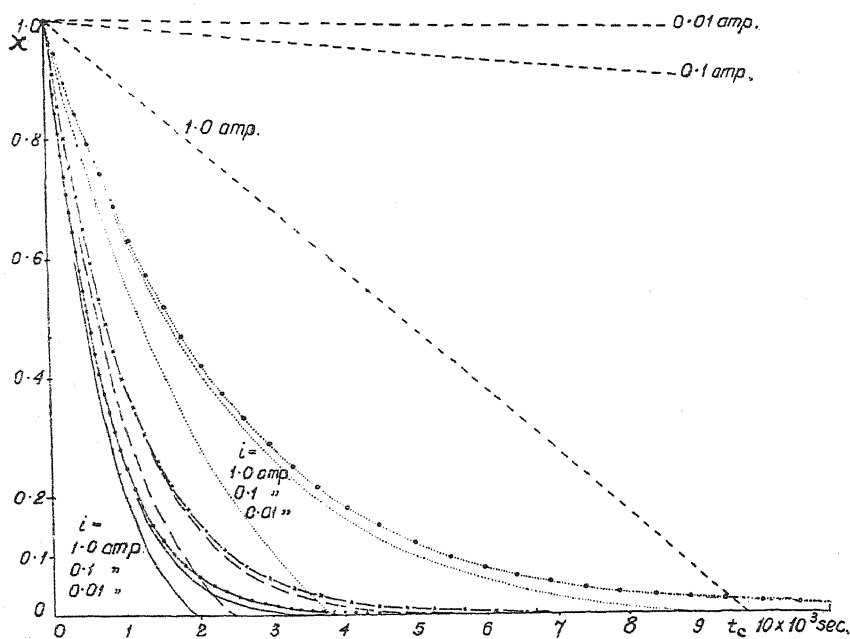


FIG. 1.—Purifying efficiency of filtration, dialysis, electrolysis and combinations of these. Concentration after t_c seconds of purification as a fraction (X) of the initial concentration.

———— F.D. F.D. ----- E.
 ----- E.F. × × × × F.
 E.D. ○ ○ ○ ○ ○ D.

TABLE I.—THE PURIFICATION TIMES

(in seconds).

$c_e^0 = 10^{-3}$ gm. equiv./c.c. (i.e., 1 N.).

Final Concentration of the Foreign Electrolyte, c_e	$= 10^{-1} c_e^0$.	$= 10^{-2} c_e^0$.	$= 10^{-3} c_e^0$.	$= 10^{-5} c_e^0$.
$i = 1.00$ amp. } E.F.D.	1328	1850	1933	1940
$= 0.10$ " } E.F.D.	1641	2970	3500	3590
$= 0.01$ " } E.F.D.	1684	3340	4670	5200
$i = 1.00$ amp. } E.F.	1773	2368	2450	2460
$= 0.10$ " } E.F.	2336	4138	47.21	4811
$= 0.01$ " } E.F.	2443	4796	6569	7256
$i = 1.00$ amp. } E.D.	3039	3695	3831	3841
$= 0.10$ " } E.D.	4977	8005	8723	8817
$= 0.01$ " } E.D.	5385	10,363	13,395	14,194
(F.D.)	1690	2×1690	3×1690	5×1690
(F.)	2450	2×2450	3×2450	5×2450
(D.)	5450	2×5450	3×5450	5×5450
$i = 1.00$ amp. } E.	8685	9553.5	9640.35	9649.23
$= 0.10$ " } E.	10×8685	10×9553.5	10×9640.35	10×9649.23
$= 0.01$ " } E.	100×8685	100×9553.5	100×9640.35	100×9649.23

decreased, the current would, of course, also decrease exponentially, and a considerably less effective purification by electrolysis would result, even at very low electrolyte concentration.

By taking unity as the time required to attain a given final concentration by dialysis, we can give an order of efficiency of the other six purification methods for any given value of (arbitrarily adjustable) current strength or filtration pressure; this order is not, however, in the case of any of the electrical methods, independent of the initial concentration of the foreign electrolyte, as is clearly shown by Table II.

TABLE II.—THE RELATIVE PURIFICATION TIMES.

(Purification Times for Dialysis taken as 1.)

$$i = 0.01 \text{ amp. } p_e - p_a = 10^3 \text{ gm./cm.}^2$$

Initial Concentration : Final Concentration :	10^{-3} 10^{-8}	10^{-3} 10^{-6}	10^{-6} gm. equiv./c.c. 10^{-8} gm. equiv./c.c.
E.F.D. . . .	5.24	3.26	20.6
E.F. . . .	3.76	2.28	15.9
F.D. . . .	3.22	3.22	3.22
F. . . .	2.22	2.22	2.22
E.D. . . .	1.92	1.05	13.60
D. . . .	1.00	1.00	1.00
E. . . .	0.028	0.014	12.30

Discussion.

(a) The contribution of electrolysis to the purification resulting from filtration or dialysis is only material when the current strength employed is large compared with the original concentration of contaminant. When, however, the electrolyte content is large, heavy currents cannot generally be used, because the solution would heat up far too much while small currents on the other hand are comparatively ineffective. However, at quite small electrolyte concentrations a small current (0.01 amp.) is very effective; but electrolytic purification must be applied with care, owing to the tendency to disturb neutrality.

(b) If the smallest particles of the hydrosol are a hundredfold greater than in the case so far considered, then the width of the capillaries of the membrane employed can, of course, be correspondingly greater, and if we keep the thickness and porosity of the membrane the same, there will be a large increase in the water transmissivity, D , while the permeability of the foreign electrolyte (δ^*) will not be materially affected. Consequently, the degree of purification obtainable by filtration will be considerably enhanced.* Of course, a further material improvement can be attained by using a filtration pressure considerably greater than one atmosphere, or by converting the continuous filtration process into a discontinuous one.²

(c) If, however, the smallest hydrosol particles are a hundredfold smaller, the necessary decrease in the width of the membrane capillaries will involve a large decrease in the water transmissivity of the membrane, while its permeability to the foreign electrolyte will not fall to the same extent.† With very highly dispersed hydrosols, therefore, dialysis will

* A membrane with very coarse capillaries ($d = 0.87 \times 10^{-2}$ cm., $W = 0.725$, $D = 8900 \times 10^{-7}$, $\beta_s = 228 \times 10^{-7}$ cm.) gave a permeability to HCl, $\delta^* = 14.1 \times 10^{-4}$ (calculated by equation (9)).

² E. Manegold and R. Hofmann, *Kolloid. Z.*, 1930, **51**, 220.

† Cellophane ($d = 0.4 \times 10^{-2}$ cm., $W = 0.595$, $D = 0.25 \times 10^{-7}$, $\tau_s = 2 \times 10^{-7}$ cm. (?) gave a permeability to HCl, $\delta^* = 2.3 \times 10^{-4}$ (calculated from results of urea dialysis).

always give quicker results than filtration, except when high-pressure filtration is applied.

(d) E. Heymann³ has put forward similar considerations as to the purifying action. The experimental arrangement on which his work is based only differs from ours in that he maintains a constant potential difference across the electrodes instead of—as we do—a constant current strength.

Heymann's calculations have rather the character of estimates, and some of the deductions are not convincing, or should be qualified by pointing out that the order of the relative purification times cannot be constant but must essentially depend on the size of the hydrosol particles, and of the foreign electrolyte molecules; and on the initial concentration of the foreign electrolyte.

The selection of the membrane is governed by the size of the smallest hydrosol particles and the size of the foreign electrolyte molecules, while the amount of electrolyte present determines whether electrolysis should be used and, if so, at what stage it should be applied.

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³ E. Heymann, *Z. physik. Chem.*, 1925, 118, 65.

PRINCIPLES GOVERNING THE PREPARATION OF MEMBRANES HAVING GRADED POROS- ITIES. THE PROPERTIES OF "GRADOCOL" MEMBRANES AS ULTRAFILTERS.

BY W. J. ELFORD.

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Artificial membranes usually have a gel structure as their basis. Those most extensively employed have been prepared from collodion, suitable films being produced by two methods.

(1) A solution of nitro-cellulose in a volatile solvent, such as a mixture of equal parts of ether and alcohol, is spread as a thin layer and exposed for the solvents to evaporate under controlled conditions of temperature and humidity. When the concentration of nitro-cellulose reaches a certain critical value, a gel film will form *spontaneously*, and may be finally equilibrated against water by washing out the remaining solvents.

(2) Alternatively a solution of nitro-cellulose in a relatively non-volatile solvent like acetic acid may be used, but in this case it is necessary to impose conditions which precipitate gelation. The acetic acid collodion, while held within the interstices of filter paper or some other suitable support, is plunged into a large excess of water. The latter gradually replaces the acetic acid through a process of inter-diffusion, and, being a non-solvent, produces a tendency to precipitation with the result that the nitro-cellulose forms a gel film, the porosity of which is determined mainly by the concentration of nitro-cellulose in the original solution. Studies of the general physical properties of films prepared by

both these methods have shown that the membranes resulting from the "spontaneous" gelling process are characterised by a superior uniformity in structure compared with those produced by "enforced" gelation.^{1a} The ultramicroscope reveals a certain granularity in the film structure formed by a linking up of elementary nitro-cellulose particles which are somewhat elongated in shape and behave as though possessed of polar properties.

Uniform Membranes of Graded Porosities.

Methods for obtaining uniform membranes from ether-alcohol collodion have been available for many years,² but provide only a limited range of low porosities. Such membranes are excellent for diffusion and dialysis operations, and also for measurements of the osmotic pressures of colloids. However, in order that the systematic analysis of colloiddally dispersed systems may be undertaken by means of fractional ultrafiltration, uniform reproducible membranes of graded porosities ranging from 1μ down to molecular dimensions are required. The acetic acid collodion membranes³ cover this range of porosities but individually these membranes do not possess the requisite uniformity of pore size. The graded collodion ("gradocol") membranes described by Elford^{1b} were evolved to meet more adequately the requirements of ultrafiltration analysis. Preliminary observations on various types of collodion films made it evident that in order to produce a series of uniform membranes having graded porosities it would be necessary (1) to select such solvents as would ensure that the collodion, under appropriate conditions, should undergo *spontaneous gelation* and (2) to secure a means of varying the state of aggregation of the nitro-cellulose at the instant when "setting" occurred. The solvent in the collodion from which "gradocol" membranes are prepared contains four essential components, ether, alcohol, acetone and amyl alcohol. The ether and alcohol ensure a strong gelling tendency, and the acetone and amyl alcohol, through the mutual antagonism in solvent action towards nitro-cellulose manifested by these liquids when present in suitable relative proportions, provide a means of controlling the aggregation factor in membrane formation. When preparing a membrane the collodion is poured into a flat glass cell to form a uniform layer about 1.5 mm. in thickness, and then exposed in a still atmosphere at constant temperature and humidity. The subsequent evaporation of the solvents is a very complex process and to assess the composition of the system at any moment is practically impossible. However, the important happenings within the collodion layer are that the concentration of nitrocellulose increases progressively owing to the evaporation of the more volatile components, acetone, alcohol and particularly the ether, while, at the same time, the proportion of the non-volatile constituent amyl alcohol gradually rises. In consequence of this latter effect conditions are slowly approached when the antagonism between amyl alcohol and acetone may become prominent and implement a process of aggregation among the nitro-cellulose particles. The concomitant increase in concentration, however, advances the incidence of "setting," i.e. the linking up of the particles or aggregates to form the porous matrix. The interrelation of these two processes determines the character of the final membrane. Thus the more advanced the state of aggregation at the time of "setting," the more porous is the film.

The "parent collodion" for the gradocol membranes, starting with the

¹ (a) Elford, W. J., *Proc. Roy. Soc., B*, 1930, **106**, 216. (b) *J. Path. and Bact.*, 1931, **34**, 505. (c) *Proc. Roy. Soc., B*, 1933, **112**, 384.

² (a) Bigelow, S. L., and Gemberling, A., *J. Amer. Chem. Soc.*, 1907, **29**, 1576. (b) Bartell, F. E., and Carpenter, D. C., *J. Physic. Chem.*, 1923, **27**, 101. (c) Bjerrum, N., and Manegold, E., *Koll. Z.*, 1927, **43**, 5. (d) Pierce, H. F., *J. Biol. Chem.*, 1927, **75**, 795.

³ Bechhold, H., *Z. physik. Chem.*, 1907, **60**, 257.

commercial "Necol" solution 356A/9 (a concentrated solution of nitro-cellulose in a mixture of equal parts of alcohol and ether made by Nobel Chemical Finishes, Ltd.), is described as an N8/40 (1:9) system. This signifies that 8 g. of amyl alcohol are added per 40 g. of "stock Necol" (commercial 356A/9 collodion diluted with an equal weight of acetone), and this mixture is then diluted with its own weight of a mixture of alcohol (1 part) and ether (9 parts). Such a parent collodion prepared with dry solvents usually yields a membrane of average pore diameter (A.P.D.) 0.6 to 0.8 μ . Reference should be made to the original paper^{1b} for details of the conditions and technique for preparing the membrane. More porous membranes are obtained by promoting the aggregation tendency in the system, and this is accomplished by adding to the parent collodion small amounts, up to 5 per cent., of a non-solvent, *e.g.* water. Membranes, having progressively lower porosities result when the aggregation tendency is suppressed as when similar small percentages of a good solvent, *e.g.* acetic acid or ethylene-glycol-monoethyl-ether, are incorporated. In this manner uniform membranes with graded porosities covering the wide range from 2 μ down to molecular dimensions may be produced. Membranes comparable with those obtained from "Necol" can also be prepared from Schering "Celloidin," while the American workers, Bauer and Hughes⁴ have successfully employed two different brands of "Parlodion" (Du Pont and the Mallinckrodt Chemical Works). Thus it is now possible for workers in different laboratories, often with different starting materials, to prepare comparable series of graded membranes. The good reproducibility now to be attained in experimental conditions for membrane studies is reflected in the excellent agreement among the ultrafiltration results obtained by independent investigators.

Comparison of the General Influences Exerted on Membrane Characteristics by the Incorporation of Various Liquids in the "Parent Collodion."

The interpretation entertained of the respective modes of action of solvents and non-solvents in modifying the porosity of the membrane furnished by the "parent collodion" was thought to merit a more extensive examination to test further its general applicability. Accordingly the influence exerted by a number of liquids which were known to possess individually varying degrees of solvent power for nitro-cellulose were studied. An index of their solvent powers and compatibilities in the presence of the basic components alcohol, ether and acetone was obtained from their respective "water tolerance" values, *i.e.* the amount of water (perfect non-solvent) necessary to discharge the solvent ability of a given volume of the liquid under certain arbitrarily chosen standard conditions (see Table I.). For these tests 2 per cent. solutions of dried shreds of Schering "Celloidin" in (a) Acetone, (b) Alcohol:Ether = 1:1, and (c) Alcohol:Ether:Acetone = 1:1:2 by weight were used. Then 3 c.c. of the collodion were titrated with water until a permanent turbidity just developed. An addition of 1 c.c. of the liquid under examination was made, whereupon the turbidity would be dispelled by a solvent and enhanced by a non-solvent. In the former case the volume of water required to restore the turbidity was determined, and is shown by the figure given on the left-hand side of each column in Table I. In instances of increased turbidity by non-solvents, the addition of 1 c.c. of liquid was made initially to the 3 c.c. of collodion. The volume of water necessary to produce turbidity would in consequence be reduced, and by an amount which, expressed as a negative quantity, served as an index of the "precipitating power" possessed by non-solvents. The figures given on the right hand of each column in Table I. were determined in this way, but it is interesting to note that not

⁴ Bauer, J. H., and Hughes, T. P., *J. Gen. Physiol.*, 1934, 18, 143.

TABLE I.—SOLVENT ACTION SHOWN BY VARIOUS LIQUIDS TOWARDS NITROCELLULOSE AS INDICATED BY WATER TOLERANCE VALUES.

Liquid.	Water Tolerance (in c.c.) per 1 c.c.			Remarks.
	Acetone Collodion.	Alcohol : Ether Collodion.	Alcohol : Ether : Acetone (1 : 1 : 2) Collodion.	
Acetone . . .	0.20	0.13	0.18	A good solvent in each case.
Ethyl Alcohol	0.15	P.T. 0.20	0.08	A good solvent in presence of ether or acetone. Acting alone it is a non-solvent.
Ether . . .	0.24	0.23	0.18	A good solvent in each case in moderate concentration—when the proportion of ether is high its behaviour simulates that of a non-solvent and titration of the system with water is complicated by emulsion formation.
Methyl Alcohol	0.03	P.T.	P.T.	An indifferent solvent—functions mainly as diluent only.
Ethylene glycol mono-ethyl ether	0.22	0.29	0.05 — 0.02	An excellent solvent in each case.
Ethylene Glycol	I.T. — 0.25	I.T. — 0.13	I.T. — 0.23	Behaves as a non-solvent in each case.
Acetic Acid .	0.14	0.18	0.10	A good solvent generally.
Amyl Alcohol	0.25	P.T. 0.20	0.22	A good solvent in moderate concentration in presence of acetone or ether-alcohol, but as its concentration relative to acetone increases it eventually behaves as a precipitant, while under similar conditions in presence of ether-alcohol it produces clear gel. Alone it is a non-solvent.
Ethyl Acetate	0.17	0.10	0.18	A good solvent generally.

P.T. = permanent turbidity.

I.T. = increased turbidity.

all the values are negative. Genuine non-solvents yield negative values, but the positive figures are given by those liquids, which, although they could not re-dissolve the precipitate when added alone to the turbid system, when operating in conjunction with a complementary liquid were able to function as good solvents, *e.g.* ethyl alcohol with ether. Acetone, ethylene-glycol-monoethyl-ether, acetic acid and ethyl acetate behaved consistently as good solvents, while ethylene glycol was a non-solvent. Ether functioned as a good solvent in moderate concentrations with acetone or alcohol, but if its proportion was increased beyond certain limits precipitation occurred. Methyl alcohol was a very indifferent solvent, appearing to act mainly as a diluent only. The behaviour of amyl alcohol was of particular interest in view of the fact established earlier that when its concentration in relation to acetone exceeded a certain value precipitation of the nitro-cellulose occurred. Under the prevailing standard conditions for which the figures of Table I. hold, amyl alcohol appeared to be quite a good solvent. Knowing that during the process of membrane formation the proportion of amyl alcohol to acetone at the start is 8 : 20, and thereafter gradually increases, a more detailed study was made on collodions containing different fractional

proportions of amyl alcohol. In the presence of acetone the proportion of amyl alcohol had to be at least 50 per cent. before any appreciable antagonistic influence was shown by reduction in water tolerance. The viscosity of the collodion increased noticeably as the amyl alcohol was further increased until finally precipitation of nitro-cellulose occurred with the proportion of 80 per cent. A parallel experiment with ether-alcohol collodion showed that in this case the presence of 50 per cent. amyl alcohol produced a definite increase in viscosity which became greater on adding water until the system became biphasic consisting of a clear transparent gel and viscous solution. When the proportion of amyl alcohol was increased further to 75 per cent., the gel separated in the collodion itself. On standing such a system forms a clear semi-rigid gel. The contrast between the behaviour of systems containing acetone and those without was clearly demonstrated by these experiments. The aggregation in the presence of acetone proceeds to the stage of visible precipitation of nitro-cellulose, while with alcohol and ether aggregation only to the point of gelation occurs. Presumably the nitro-cellulose remains in a highly solvated state in the latter instance, whereas when acetone is present desolvation more readily occurs and the aggregation

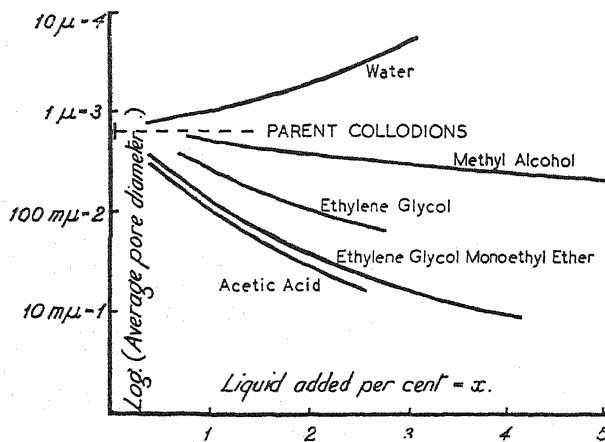


FIG. 1.—Curves showing how the membrane porosity varies with various liquids are incorporated in the Parent Collodion.

Systems = N8/40 (1:9) + x

may proceed until precipitation sets in. It is this possibility of advanced aggregation during the formation of the membrane that imparts to gradocol membranes much greater porosities than can be obtained from ether alcohol collodion only. Furthermore, the gradual manner in which the conditions favourable to aggregation are approached is undoubtedly responsible for the sustained uniformity characterising even the most porous membranes of the series.

A series of comparable collodions incorporating in turn each of the several liquids mentioned in Table I. and having the composition N6/40 (X:9) was prepared. Here "X" serves to indicate that the 1 part by weight of alcohol used in the normal "parent collodion" was substituted by the same weight of each of the aforesaid liquids. This quantity constituted nearly 5 per cent. of the solution so that the influence exerted by each substituent should be well defined. Membranes from each system were prepared under similar known conditions, and their characteristics are summarised in Table II. For comparison also the curves of Fig. 1 have been constructed from the results obtained with other collodions, in order to show how the magnitude of the change in membrane porosity depends on the amount of liquid added to the normal parent collodion.

It will be seen that general support is given to the hypothesis already advanced that the addition of a good solvent favours dispersion and gives a less porous membrane, while a non-solvent increases the tendency towards aggregation and in consequence the porosity becomes greater. There is an exception, however, in the case of ethylene glycol, which, although behaving ordinarily as a non-solvent, produces a definite decrease in membrane porosity. It had been anticipated that the addition of this liquid would give a more porous membrane, as happens in the case of ether alcohol collodion.^{2d} Its anomalous behaviour in the present more complex solvent was found to be due to its influence upon the aggregation process determined by the amyl alcohol and acetone present. It was found that the precipitate produced by adding amyl alcohol to acetone collodion was quickly dissolved on adding a little ethylene glycol. Thus the aggregating tendency is counteracted by ethylene glycol which assists the gelation. The reason for the observed decrease in membrane porosity therefore becomes apparent, and the importance of the interaction between the amyl alcohol and acetone as being the prime factor determining the aggregation receives new emphasis.

TABLE II.—INFLUENCE EXERTED BY VARIOUS SUBSTITUENTS IN "PARENT COLLODION" UPON CHARACTER OF MEMBRANE.

Collodion System N.6/40 (X: 9).	Viscosity 20° C. Pois.	Evaporation Period, mins.	Membrane Thickness, mm.	Specific Water Content,	A.P.D. μ.	Remarks.
X =						
Ethyl Alcohol	11.80×10^{-2}	90	0.17	0.80	700	Good membrane.
Acetone	13.45×10^{-2}	100	0.13	0.69	380	Slight deposit in cell. Had not set at 90 mins.
Ether	13.17×10^{-2}	90	0.12	0.70	400	Slight deposit in cell— membrane not uniform.
Methyl Alcohol	13.78×10^{-2}	90	0.16	0.77	600	Good membrane.
Ethylene glycol mono-ethyl ether	14.68×10^{-2}	120	0.04	0.33	1.2	Good membrane—quite transparent. Porosity so low that calibration was difficult.
Ethylene Glycol	19.11×10^{-2}	100	0.18	0.81	220	Good membrane.
Acetic Acid	15.75×10^{-2}	120	0.05	0.53	5.5	Good membrane but had not set in 100 mins.
Amyl Alcohol	13.11×10^{-2}	100	0.16	0.80	960	Good membrane—had not set in 90 mins.
Ethyl Acetate	14.09×10^{-2}	90	0.14	0.76	360	Good membrane.
Water	14.31×10^{-2}	90	0.2 (ca.)	?	3000 (ca.)	Deposit in cell—uneven surface—accurate calibration not possible.

In each case 50 c.c. of collodion were poured into a cell 20 cm. in diameter.

Temperature = 22.5° C. Measurements by Mr. S. Jacobs.

The Uniformity of Pore Size and Structure in Gradocol Membranes.

Successful ultrafiltration analysis depends largely upon the degree of uniformity in pore size and structure characterising individual membranes. A convenient criterion of this degree of uniformity is afforded by the ratio of the maximum pore size (from the critical air pressure) to the average pore size (from the rate of flow of water), and this is found to be as 2 : 1 for gradocol membranes. Recently Grabar and Nikitine⁵ have determined experimentally the dispersion curves for the distribution of pores in membranes of different porosities using the method due to Erbe.⁶ Their measurements indicate the relation of the true mean pore size to the maximum pore size for gradocol membranes to be rather better than 1 : 2, and in addition serve to emphasise the fact that the average pore diameter calculated from rate of flow of water measurements does not in general represent the true mean size of the largest and smallest pores but rather a "statistical average." This point has been well discussed by Ferry.⁷

"Gradocol" membranes are graded in terms of their average pore diameter given by the rate of flow of water method, which provides a uniform basis of calibration for the complete series. The technique of calibration has been fully described in earlier papers^{1b, 8b} where a discussion of the assumptions regarding the membrane structure will also be found.

It is essential that the degree of uniformity in pore size possessed by these membranes as well as the basis of their calibration be appreciated when considering their behaviour as ultra-filters.

The Behaviour of Gradocol Membranes as Ultrafilters.

During the past five years "gradocol" membranes have been extensively used as ultra-filters in acquiring knowledge of the particle sizes in disperse systems, e.g. viruses, bacteriophages, proteins, toxins, and enzymes. When using an ultra-filter to estimate the particle size of an unknown suspension it is not sufficient to regard the membrane as functioning just like a sieve where size of mesh alone matters. The pores of a membrane may be anything from 100 to 10,000 times as long as they are wide, and since their diameters are of microscopical or ultramicroscopical dimensions the importance of surface equilibria is no longer negligible. On the contrary under certain circumstances such equilibria may dominate the process of filtration. It becomes imperative therefore to study each disperse system carefully, having regard especially to its stability and the surface equilibria when in contact with the membrane. Such factors as the nature and p_H of the medium, the filtration pressure and the concentration of the disperse phase are each of importance in the filtration. Experience with viruses, phages and proteins has shown that extremely favourable conditions for filtration obtain when Hartley's broth at p_H 7.6 is used as medium. This liquid is an extract of digested animal tissue, and in addition to maintaining conditions suitable for the stability of virus suspensions it also contains a capillary active constituent, which has the property of reducing adsorption to a minimum and so facilitating the passage of the suspended particles through a filter. It should be pointed out that the properties of broths in this respect vary considerably according to the degree of tissue digestion permitted. If carried too far the important intermediate products, among which is the capillary active constituent, are lacking and the medium then is in no way superior for filtration purposes to normal physiological saline,

⁵ Grabar, P., and Nikitine, S., *J. chim. physique*, 1936, **33**, 721.

⁶ Erbe, F., *Koll. Z.*, 1933, **63**, 277.

⁷ Ferry, J. D., *Chem. Rev.*, 1936, **18**, 373.

⁸ (a) Elford, W. J., and Ferry, J. D., *Biochem. J.*, 1934, **28**, 650. (b) *Brit. J. Exp. Path.*, 1935, **16**, 1. (c) *Biochem. J.*, 1936, **30**, 84.

and absorption becomes considerable. Selecting in all cases those conditions deemed most favourable for filtration, the so-called "filtration end-point" is determined by filtering the system through membranes having progressively finer pores until the limiting porosity just effective in completely retaining all the disperse phase is reached. If ideal membranes having straight pores of circular cross-section were available then with knowledge of the adsorption equilibrium between the disperse phase and the filter substance it would be feasible to predict the filtration "end-point" for various sizes of particle. However such conditions do not obtain and with our still imperfect membranes and lack of precise knowledge of their structure the only practical procedure is to calibrate them in terms of their behaviour as ultra-filters for suspensions of known particle size. The problem has been discussed in an earlier paper (Elford, 1933) where the experimental data are given for bacteria, viruses, gold sols and proteins, that

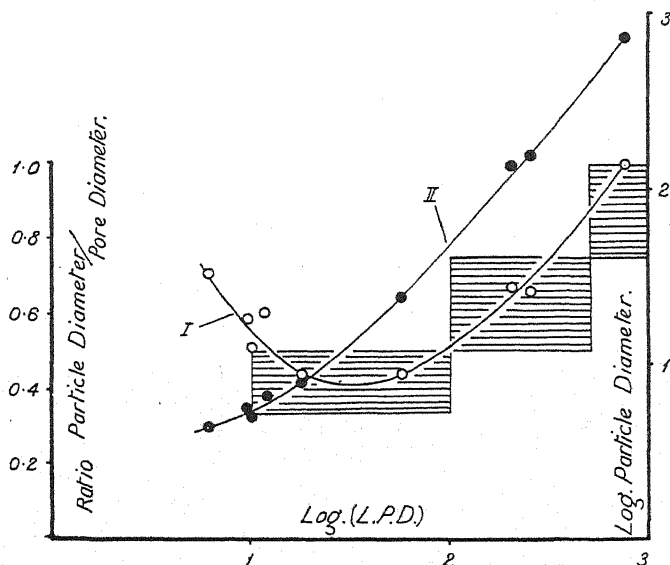


FIG. 2.—Curve I shows the relationship of the ratio particle diameter/pore diameter to the log. (limiting pore diameter). Curve II shows the relationship of the ratio of the log. (particle diameter) to the log. (limiting pore diameter).

lead to the adoption of the following values for a "factor" F enabling the particle diameter " p " to be deduced from the pore size, d , of the limiting membrane by means of the relationship

$$p = F \cdot d$$

Limiting Pore Diameter.	Factor F .
10 to 100 $m\mu$	0.33 to 0.50
100 to 500 $m\mu$	0.50 to 0.75
500 to 1000 $m\mu$	0.75 to 1.0

Since these values were first adopted evidence has accumulated upon the filterability of protein and virus systems which have also been studied by the methods of ultra-centrifugal analysis⁹ and ultra-violet light photography.¹⁰ It is now possible to construct a calibration curve based upon data for systems of comparable character—*viz.* bacteria, viruses and proteins in the same medium, Hartley's broth at p_H 7.6. Table III. gives the data from which the curves of Fig. 2 have been constructed. The ratio of

⁹ Svedberg, T., *Trans. Faraday Soc.*, 1930, **26**, 737, 740.

¹⁰ Barnard, J. E., and Elford, W. J., *Proc. Roy. Soc., B*, 1931, **109**, 360.

the particle diameter to the limiting pore diameter (L.P.D.) has been plotted against the log. (L.P.D.) in curve 1. The minimum characterising this curve in the neighbourhood of 20-30 $m\mu$ porosity might be anticipated on the grounds of our knowledge of the factors influencing the calibration of membranes in this region.^{10,7} The broad bands shaded with horizontal lines indicate the relation borne by the factor so far adopted in ultra-filtration studies to the experimental curve. Curve 2 in Fig. 2 shows how the logarithm of the particle diameter varies with the log. (L.P.D.). Ferry⁷ has compared the values of the particle sizes for many bacteriological systems given by use of the factor read directly from the experimental calibration curve with those quoted by various authors and based upon the value of the factor adopted by Elford.¹⁰ The agreement is good, particularly if for

TABLE III.—FILTRATION END-POINT DATA FOR SYSTEMS OF KNOWN PARTICLE SIZE.

System.	"End-Point" L.P.D., $m\mu$.	Particle Size, $m\mu$.	Ratio Particle Size/L.P.D.	Remarks and Authors.
B. Prodigiosus .	750	500-1000	1.0 (av.)	Microscopical measurement.
Vaccinia virus .	250	150-180	0.66 (av.)	Size by ultra-violet photography. Filtration. ¹¹
Infectious Ectromelia	200	130-140	0.67 (av.)	Size by ultra-violet light photography. ¹⁰
Hæmocyanin (Helix)	55	24	0.44	Size by ultra-centrifugal analysis. ¹² Filtration. ^{8c}
Edestin .	18	8	0.44	Size by ultra-centrifugal analysis. ¹³ Filtration. ^{8c}
Serum-Pseudo- globulin (horse)	11-12	6.9	0.60	{ Size by ultra-centrifugal analysis. ^{9, 14} Filtration. ^{8a}
Serum Albumin (horse)	9-10	5.4	0.57	
Oxyhæmoglobin	10	5	0.50	Size by ultra-centrifugal analysis. ⁹ Filtration. ¹⁰
Egg albumin .	6	4.34	0.72	Size by ultra-centrifugal analysis. ⁹ Filtration. ^{10 4}

Each system when filtered was in Hartley's broth medium at p_H 7.6-7.8.

"end-points" within 10 $m\mu$ of the porosities where a sudden change in the value of the adopted factor occurs, e.g. at 100 $m\mu$, the mean of the alternative values is used to deduce the particle size. That good agreement should exist is clear from Fig. 2 which shows the good relation between the "factor" and the experimental curve.

In practice it is not always possible to select such comparable conditions for all systems as obtain for the systems used for the purposes of calibration. In some instances there may be good approximation to such conditions, as for example with the bacteriophages, and also foot-and-mouth disease virus which is obtained in a vesicular fluid containing very little protein. The virus suspensions usually consist of extracts of ground-up infected tissue—may be brain, liver, lung, cord or tumour tissue—in various states of degeneration, sometimes to the extent of necrosis, according to the particular pathological condition. In expressing limits for the probable particle size it was intended to allow tolerance for any displacement of the "end-point" due to serious departure from the most favourable filtration





















¹¹ Elford, W. J., and Andrewes, C. H., *Brit. J. Exp. Path.*, 1932, 13, 36.

¹² Svedberg, T., and Chirnoaga, E., *J. Amer. Chem. Soc.*, 1928, 50, 1399.

¹³ Svedberg, T., and Stamm, A. J., *ibid.*, 1929, 51, 2170.

¹⁴ von Mutzenbecher, P., *Biochem. Z.*, 1933, 266, 226, 250.

TABLE IV.—FROM BACTERIUM TO MOLECULE.

750 $\mu\mu$		BACILLUS PRODIGIOSUS	
350 $\mu\mu$		SPIRILLUM PARVUM	
250 $\mu\mu$		PSITTACOSIS VIRUS	
200 $\mu\mu$		SPIROCHAETA PALLIDA	
		AGALACTIA	
150 $\mu\mu$		BOV. PLEUROPNEUMONIA	
		SEWAGE MICRO-ORGANISM	
		VACCINIA	
		CANARY POX	
125 $\mu\mu$		RABIES	
		INFECTIOUS ECTROMELIA	
		HERPES	
		PSEUDO RABIES	
100 $\mu\mu$		INFLUENZA	
		BORNA DISEASE	
		NEWCASTLE DISEASE	
85 $\mu\mu$		VESICULAR STOMATITIS	
75 $\mu\mu$		ROUS SARCOMA	
		FOWL PLAGUE	
		PHAGES STAPH'K', C16, D4, D12	
		PHAGES D54, S41, MEGATHERIUM	
		RIFT VALLEY FEVER	
		EQUINE ENCEPHALITIS	
		TOBACCO MOSAIC	
		ST. LOUIS ENCEPHALITIS	
		PHAGES, TYPHOID TIII, C36, D13, D20, D48	
		HAEMOCYANIN HELIX	
		YELLOW FEVER	
		LOUPING ILL	
		PHAGE S13	
		POLIOMYELITIS	
		FOOT & MOUTH DISEASE	
		EDESTIN	
		SERUM GLOBULIN	
		SERUM ALBUMIN	
		OXYHAEMOGLOBIN	
		EGG ALBUMIN	
			75 $\mu\mu$
			60 $\mu\mu$
			35 $\mu\mu$
			30 $\mu\mu$
			25 $\mu\mu$
			22 $\mu\mu$
			17 $\mu\mu$
			10 $\mu\mu$
			8 $\mu\mu$
			5 $\mu\mu$
			4 $\mu\mu$

conditions. However any such influences may be minimised by adopting a procedure of systematic fractional filtration.

Table IV. summarises the particle diameters of viruses and bacteriophages determined by ultra-filtration analysis with gradocol membranes in this and other laboratories. The mean of the probable size values is given in each case. The figures included for the proteins are essentially those found by Svedberg and his co-workers (*cf.* Table III.).

General confirmation has been accorded to the findings of ultra-filtration analysis by recent centrifugation results in this field (lack of space prevents their review here) and in several instances among the larger viruses (100 m μ in size and over) by ultra-violet light photography. The success that has attended the use of gradocol membranes as ultra-filters must undoubtedly be attributed to the degree of uniformity of pore size in individual membranes, and also to the fact that the consistent use of Hartley's broth at p_H 7.6, although not an ideal simple medium, has provided conditions, which, for the systems in question, are most favourable for filtration. In this medium variations due to differences in specific adsorption and stability, and sensitiveness to changes in p_H , which in simple aqueous media would most certainly become evident, are eliminated, thereby permitting a reliable comparison of filtrabilities.

Among other purposes for which this series of membranes has been profitably applied may be mentioned the concentration and purification of viruses, bacteriophages, hormones, toxins and enzymes upon membranes of suitable porosities. Further as a tool in routine bacteriology, *e.g.* for sterilisation of fluids, resolution of mixed cultures, etc.—the membranes have proved invaluable.

Summary.

(1) The general principles determining the formation of collodion membranes having graded porosities are discussed with reference in particular to the series of "gradocol" membranes.

(2) The behaviour of these membranes when they are used as ultra-filters in determining the particle sizes of disperse systems is reviewed. The derivation, significance and general dependability of the "factor" employed in deducing the particle diameter of a suspension from the limiting pore diameter just able to retain all the disperse phase have also been discussed.

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GENERAL DISCUSSION.*

Dr. P. Grabar (*Paris*) said: In comparison with previously used ultrafilters, the "Gradocol" membranes show great progress; in my ultrafiltration experiments¹ I have used "gradocol" membranes of my own preparation. But, as we have shown recently² these membranes still present some imperfections: their structure is not quite homogeneous and they have a certain "dispersion in the size of their pores." It is most probable that dispersion is due to the irregularity of the structure, and it would be satisfactory to be able to prepare more adequate membranes.

One may presume, as Elford has noted, that in a gel which is formed gradually and slowly, the disposition of the particles is not haphazard.

*On 2 preceding papers.

¹ *C. R. Ac. Sc.*, 1934, **198**, 1640; 1935, **200**, 1795 (with A. Riegert); *C. R. Soc. Biol.*, 1934, **116**, 72; 1934, **117**, 700 (with A. Koutseff); 1935, **118**, 455; 1936, **121**, 1472. *Bull. Soc. chim. biol.*, 1936, **18**, 1192 (with A. Riegert).

² P. Grabar and S. Nikitine, *J. Chim. physique*, 1936, **33**, 721; P. Grabar and J. A. de Loureiro, *ibid.*, 1936, **33**, 815.

Therefore, for the preparation of a good membrane it is essential to obtain first of all regular gels, and to conserve this regularity during the "hardening" of the gel by the water.

With this in view, we have, in collaboration with J. A. de Loureiro, made some experiments the results of which will be published soon. We sought to obtain membranes without macroscopical "polygonal structure" due to the "whirlpools of Benard" during the evaporation; moreover, we have avoided adding to the collodion solution any substances which could produce precipitation of nitrocellulose within the gel. We have also endeavoured to diminish the contraction of the gel, during the hardening by the water, by the choice of an adequate composition of the collodion solutions.

We studied the gelation of very simple systems, containing generally only three constituents (the systems used in the preparation of "gradocol" membranes are much more complicated, having at least 5 constituents), in order to follow the action of each of them. We thus obtained excellent membranes. We observed:

(1) To avoid the formation of "polygonal structures" we have, (a) abandoned the use of ether as solvent, because of its rapid evaporation, which produces pronounced whirlpools, and (b) evaporated very slowly by covering the evaporation-cell with a cover the upper part of which is constituted by a filter paper. This procedure gives more homogeneous gels.

(2) The different liquids used for the preparation of membranes can be roughly classified into four groups: (a) "*Perfect solvents*," e.g., ethyl acetate, which easily dissolve nitrocellulose; these give a *transparent film* when evaporated freely in the air. (b) "*swelling solvents*," e.g., acetone, which dissolve nitrocellulose more slowly; these solutions give *opaque films*. (c) "*Gelifying liquids*" such as ethyl and propyl alcohol, which do not dissolve nitrocellulose, but can be added in large quantity to solutions of nitrocellulose without causing precipitation. (d) "*Pre-precipitant liquids*," such as water.

There are, obviously, some liquids with intermediary properties, e.g., the higher alcohols which can be classified between c and d.

(3) In order to prepare a gel (and not a film) it is necessary to have nitrocellulose solutions containing one of the "gelifying liquids." The proportion of the latter regulates the swelling of the gel and consequently the water content and the thickness of the membrane.³ The same percentage of the "gelifying liquid" in the initial solution gives membranes of equal swelling. We chose propyl alcohol, because it is less volatile and therefore the ratio propyl alcohol/nitrocellulose changes but little in the course of evaporation.

(4) When the solution is prepared with "a perfect solvent" the membranes will be "tight" (of low permeability) whilst with a "swelling solvent" they will have a large porosity. One supposes this effect to be due to a different state of aggregation of the particles of nitrocellulose.

Membranes of different porosities can be prepared by using two different initial solutions: one made with a "perfect solvent" and the other with a "swelling solvent"; these solutions will give membranes of extreme porosities. Membranes of intermediate porosities can be obtained either by addition to the initial solutions of small quantities of solvents of the opposite group (but of a higher vapour tension), or by mixtures of different proportions of the two initial solutions (in this case it is necessary to use solvents having nearly the same vapour tension).

(5) The evaporation must be stopped only when the gel is well formed. This is very important because if the evaporation is stopped sooner the water will precipitate the nitrocellulose in the interior of the gel and the structure of the membrane will not be homogeneous.

³ H. F. Pierce, *J. biol. Chem.*, 1927, **75**,¹795, has pointed this out in the case of ethyl alcohol.

(6) Liquids which are soluble in water only to a small extent (like amyl alcohol) should be avoided because their elimination from the membrane necessitates many and prolonged washings. Moreover, it seems to us that their presence in the gel gives place to a greater contraction when the membrane is "hardened" by the water.

Dr. W. J. Elford (*London*) said: Dr. Grabar's studies of the distribution of pores in collodion films from relatively simple systems may throw fresh light on the factors determining the uniformity of pore size and point the way whereby to obtain membranes approaching more closely the ideal of isoporosity than do those at present available. It is of course known that films of excellent uniformity may be prepared from much simpler systems than that employed in preparing the "gradocol" series. However, the available range in porosities consistent with the fulfilment of the requirements in physical properties demanded for a satisfactory ultrafilter membrane—(1) uniformity of pore size, (2) adequate mechanical strength, (3) reproducibility—is usually too restricted.

The macroscopical polygonal pattern is characteristic of the more porous films. It is developed potentially quite early in the evaporation process and may be observed, through local differences in refractivity, by viewing the film in the direction of glancing incidence to the surface. Initially it is essentially a surface phenomenon resulting, it is suggested, from the grouping of associated nitrocellulose micelles as the concentration in the surface layer increases through the rapid evaporation of solvent. If the rate of evaporation is retarded, as may be effected by placing a coarse muslin screen over the guard which surrounds the cell in which the film is prepared, then the phenomenon is subdued as the restoring influences of diffusion within the liquid layer are able to exert their effect. Early experiments of my own indicated that while through retardation of the evaporation with consequent prolongation of the period necessary for the film to set the polygonal pattern was noticeably suppressed, yet no appreciable improvement was reflected in the uniformity of pore size in the resulting membrane as measured by the M.P.S./A.P.S. ratio.

Concerning the use of amyl alcohol, while admittedly it would be advantageous to be able to wash and equilibrate membranes more quickly than is the rule with the "gradocol" films (this is already possible by using dilute aqueous alcohol solutions for the initial washings) nevertheless, the very fact that this final stage in the stabilisation of the membrane structure is accomplished gradually undoubtedly constitutes a factor contributing the uniformity of the porosity in the film.

THE THEORY OF MEMBRANE EQUILIBRIUM.

BY G. S. ADAIR.

Received 25th March, 1937.

The theory of membrane equilibrium in its most general form was established by Gibbs.¹ He showed that if a fluid mass be divided into two parts by a rigid diaphragm, permeable by some of the components but impermeable by others, the conditions that are necessary for equilibrium can be stated as follows. In the first place, the absolute temperature T' in the fluid phase designated L' must be the same as the temperature T'' in the phase L'' on the opposite side of the membrane. In the

¹ J. W. Gibbs, *Trans. Conn. Acad.*, 1876, 3. 108. *Collected Works*, 1. *Thermodynamics*, New York, 1928.

second place, the partial free energy or chemical potential of each one of the substances which are free to diffuse across the membrane must be the same in both phases. The potentials and other properties of the substances designated $S_1, S_2 \dots S_n$ are distinguished by subscripts as in formula 1.

$$\mu_1' = \mu_1'', \quad \mu_2' = \mu_2'' \quad \dots \quad (1)$$

μ_1' = the chemical potential of the substance S_1 in the phase L' . Equations of this form, which must apply to the potentials of all of the substances that can diffuse across the membrane, serve as exact thermodynamic criteria for equilibrium.

The conditions for equilibrium across the membrane differ from the conditions for two phases in contact, in that the hydrostatic pressures P' and P'' are not necessarily equal, and the potentials of the substances which cannot penetrate the membrane, S_p, S_q , etc., are not necessarily equal.

The condition for the equilibrium of charged ions, which can diffuse across the membrane subject to the restriction that an equivalent amount of an ion of opposite sign diffuses across, is given by formula 13.

Donnan and Guggenheim² and Donnan³ have shown that Gibbs' conditions for equilibrium can be expressed in terms that are more accessible to experimental investigation, by means of their formula numbered 2 below.

$$\mu_1 = \mu_1^*(T) + P v_1^* (1 - \frac{1}{2} \kappa_1 P) + RT \ln N_1 f_1 \quad \dots \quad (2)^4$$

$\mu_1^*(T)$ = a constant at a constant temperature, which need not be determined. P = the pressure in the solution. v_1^* = the volume occupied by 1 mol. of S_1 in a very dilute solution at zero pressure. κ_1 = the compressibility of S_1 in a very dilute solution. R = the gas constant. T = the absolute temperature. N_1 = molar fraction = mols. of S_1 divided by total number of mols. in the solution. f_1 = the activity coefficient which may be a measure of the deviations from the ideal solution laws. The product $f_1 N_1$ = the activity⁵, a_1 . The symbol f_1 denotes the activity coefficient at pressure P .

According to Raoult's law, the vapour pressure p_1 of the substance S_1 is approximately proportional to the molar fraction of N_1 in the solution. The potential of S_1 in a gas phase may be calculated by the formula $v_1 dp_1 = d\mu_1$, where $v_1 = RT/p_1$, for an ideal gas, and by integration $\mu_1 = RT \ln p_1 + \text{constant}$. It may be assumed that in an ideal solution, $\mu_1 = RT \ln N_1 + \text{constant}$, if the pressure on the solution be constant.

The effect of pressure on the potential of S_1 in a dilute solution may be calculated assuming that the partial molal volume $v_1 = v_1^* (1 - \kappa_1 P)$. By integration $\mu_1 = P v_1^* (1 - \frac{1}{2} \kappa_1 P)$ plus a constant. In concentrated solutions (where v_1 = the observed partial molal volume at pressure P), $RT d \ln f_1 / dP = v_1 - v_1^* (1 - \kappa_1 P)$.

² Donnan and Guggenheim, *Z. physikal. Chem.*, 1932, **162**, 346.

³ Donnan, *ibid.*, 1934, **168**, 369.

⁴ Formula 2 is subject to a small correction for the effects of changes in compressibility at very high pressures.

⁵ Complete definitions of N , f and a may include specifications of the components chosen in particular problems and also "standard states" where a and f equal unity. See Lewis and Randall, *Thermodynamics*, 1923; Gatty, *Phil. Mag.*, 1934, **2**, **18**, 273; also refs. 22 and 23 below.

Donnan and Guggenheim obtained formula 3 from 1 and 2, eliminating the constant term $\mu_1^*(T)$ which must be the same in both phases.

$$Pv_1^*(1 - \frac{1}{2}\kappa_1 P') + RT \ln N_1' f_1' = RT \ln N_1'' f_1'' + P''v_1^*(1 - \frac{1}{2}\kappa_1 P'') \quad (3)$$

They suggested an abbreviated notation in which $[v_1]$ represents

$$v_1^*[1 - \frac{1}{2}\kappa_1(P' + P'')],$$

the volume at the mean pressure $\frac{1}{2}P' + \frac{1}{2}P''$. In order to allow for the changes in compressibility with increasing pressure, the symbol $[v_1]$ is here defined by the formula

$$[v_1] = (\int v_1 dP)/(P' - P'') \quad (4)$$

where v_1 denotes the volume occupied by 1 mol of S_1 in a very dilute solution. With this definition, the formulæ 5, 6, 7, 9, 10 and 11 below are exact.

$$(P' - P'')[v_1] + RT \ln N_1' f_1' = RT \ln N_1'' f_1'' \quad (5)$$

If the substance S_1 be the solvent water, it may be more convenient to use the osmotic coefficients g_1' and g_1'' as a measure of the deviations from the ideal solution laws.

$$(P' - P'')[v_1] + g_1' RT \ln N_1' = g_1'' RT \ln N_1'' \quad (6)$$

Equations like 3 and 5 can be applied to any non-electrolyte that can diffuse across the membrane.

$$(P' - P'')[v_2] + RT \ln N_2' f_2' = RT \ln N_2'' f_2'' \quad (7)$$

It is possible to eliminate the pressures, using equations 5 and 7, as described by Donnan and Guggenheim, who obtained

$$(N_2' f_2')/(N_1' f_1')^r = (N_2'' f_2'')/(N_1'' f_1'')^r,$$

where r is $[v_2]/[v_1]$.

A slight modification of their treatment is given below, with special reference to systems in which the pressures can be determined with greater accuracy than the molar fractions, in order to obtain exact formulæ expressed in terms of the molalities of the substances, and the terms h_1 , h_2 , etc., defined by:

$$h_1 = [v_1](P' - P'')/RT \quad (8)$$

Formula 5 can then be restated in an abbreviated form

$$N_1' f_1' e^{h_1} = N_1'' f_1'' \quad (9)$$

$$e^{h_1} = (1 + h_1 + \frac{1}{2}h_1^2 + \dots)$$

A similar formula can be applied to the substance S_2 , and in a system where S_1 and S_2 can diffuse across the membrane

$$N_2' f_2' e^{h_2}/N_1' f_1' e^{h_1} = N_2'' f_2''/N_1'' f_1'' \quad (10)$$

In aqueous solutions, the molality m_2 expressed in g. mols. of S_2 per 1000 g. water, is equal to $N_2/55.51 N_1$, and it follows that

$$m_2' f_2' e^{h_2}/f_1' e^{h_1} = m_2'' f_2''/f_1'' \quad (11)$$

In practical applications of the theory of membrane equilibrium it is customary to use a simpler, approximate formula

$$m_2' f_2' = m_2'' f_2'' \quad (12)$$

Estimates of the errors due to the omission of the terms e^{h_1} , e^{h_2} , f_1' and f_1'' are given below. In the case of water $[v_1] = 0.018$ litres at low

pressures and $RT = 22.4$ litre atmospheres at 0°C. , and therefore $h_1 = 0.0008$ and $e^{h_1} = 1.0008$ at a pressure of one atmosphere. In the case of sucrose $[v_2]$ is approximately 0.21 litres, the term $e^{h_2} = 1.0096$ at one atmosphere pressure, and the approximate formula expressed in terms of the activities $a_2' = a_2''$ then differs from the exact formula $a_2'e^{h_2} = a_2''$ by about 1 per cent. The molal volume of serum albumin is approximately 54 litres, or 76 litres including hydration, and the factor e^{h_2} for the protein S_p is therefore approximately 34 at a pressure of one atmosphere.

These calculations show that, although the terms e^{h_1} and e^{h_2} can be disregarded in investigations of the membrane equilibria of small molecules, in systems where the pressure difference $P' - P''$ is small, they may prove to be important in the interpretation of experiments with membranes permeable by large molecules, as for example in the ultra-filtration of proteins, described by Elford,⁶ and the recent experimental work of Moran⁷ on equilibria with gelatine gels and sodium chloride at pressures exceeding 2000 atmospheres.

In addition to the exponential terms, it is necessary to estimate the values of f_1' and f_1'' , the activity coefficients of water in both phases. As stated by Donnan and Guggenheim,² $\ln f_1 = (g_1 - 1) \ln N_1$. If N_1 be not far from unity, their formula can be simplified

$$f_1 = 1 + N_s(1 - g_1) \quad (12a)$$

$N_s = 1 - N_1$ = molar fraction of solutes. g_1 = the osmotic coefficient, or the ratio of the observed and "ideal" osmotic pressures.

Although the observed osmotic pressures of aqueous solutions of proteins may be considerably larger than the ideal values, the changes in f_1 , calculated by formula $12a$ are small, because N_s rarely exceeds 0.0006 . A preliminary trial with a solution containing 68 g. hæmoglobin per 100 c.c. water ($N_s = 0.00018$) gave an osmotic pressure of 865 mm. of mercury at 18°C. an osmotic coefficient of 4.7 and an activity coefficient $f_1' = 0.99933$. In the phase L'' (water), $f_1'' = 1.00$.

It can be shown by similar calculations that f_1' and f_1'' are very nearly equal in systems composed of proteins and diffusible electrolytes and non-electrolytes, when the total concentration of solutes is low, so that the simple formula 12 is nearly exact. In systems where the concentrations of diffusible substances are very high m_2'' usually exceeds m_2' , an effect which might be due to an increase in f_2' or a diminution of f_1' caused by the protein.

The molar fraction N_2' , the molality m_2' and the corrected concentration $[S_2]_c'$ (expressed in mols. of S_2 per litre of solvent) all depend upon the value assumed for the hydration of the protein. It has been observed that in systems where L'' was an aqueous solution of sodium chloride and L' contained hæmoglobin, $[S_2]_c'$ was equal to $[S_2]_c''$ over a wide range of concentrations from 0.5 to 4.0 molar, on the assumption that 1 g. hæmoglobin occupied 0.965 c.c. or 1 g. combined with 0.22 g. water.⁸ Recent investigations⁹ on the protein crystals have given slightly larger values (approximately 0.3 g. water per g. hæmoglobin) and it may be inferred that the protein causes a slight diminution in f_2' (for NaCl) when a correction is made for hydration.

⁶ This vol., p. 1100.

⁷ Moran, *Rep. Food Investigation Board* for 1935, p. 20.

⁸ Adair, *Proc. Roy. Soc. A*, 1928, **120**, 573.

⁹ Adair and Adair, *ibid. B*, 1936, **120**, 422.

The Membrane Equilibrium of Ionised Electrolytes.

In a system where an acid, a base for a salt can diffuse across the membrane, the chemical potential of the electrolyte must be the same in both phases, as stated in formula 1. If the electrolyte dissociate, yielding ν_i ions of species S_i and ν_j ions of species S_j , the diffusion of an ion is subject to the condition that an equivalent quantity of ions of opposite sign pass across the membrane in the same direction. The condition for equilibrium is that

$$\nu_i \mu_i' + \nu_j \mu_j' = \nu_i \mu_i'' + \nu_j \mu_j'' \quad (13)$$

The resemblance between this formula, due to Gibbs, and the formula of Donnan,¹⁰ $[\text{Na}]' \times [\text{Cl}]' = [\text{Na}]'' \times [\text{Cl}]''$ has been discussed elsewhere.¹¹

In a system where two ions of the same sign, S_i and S_k can diffuse across the membrane, the condition for equilibrium, formula 14, has been obtained by the method used by Gibbs, since the possible variations dm_i' and dm_k' in the composition of the phase L' are subject to the condition that $dm_i'/n_i = -dm_k'/n_k$

$$\frac{\mu_i'}{n_i} - \frac{\mu_k'}{n_k} = \frac{\mu_i''}{n_i} - \frac{\mu_k''}{n_k} \quad (14)$$

$$(\mu_i' - \mu_i'')/n_i = (\mu_k' - \mu_k'')/n_k \quad (15)$$

In a system where two salts containing the ions S_i , S_j and S_k can diffuse across the membrane, formulæ 13 and 14 are both applicable. It is possible to restate these formulæ in terms of the molar fractions, as in formula 8.

$$(N_i' f_i' e^{h_i})^{\nu_i} (N_j' f_j' e^{h_j})^{\nu_j} = (N_i'' f_i'')^{\nu_i} (N_j'' f_j'')^{\nu_j} \quad (16)$$

The activity coefficients of the individual ions can be replaced by f_{\pm} , the mean activity coefficient, as in formula 17.

$$(m_i')^{\nu_i} (m_j')^{\nu_j} e^{h_i \nu_i + h_j \nu_j} = (m_i'')^{\nu_i} (m_j'')^{\nu_j} (f_{\pm}'/f_{\pm}'')^{\nu} \quad (17)$$

If the pressure difference $P' - P''$ be small, and f_{\pm} , the activity coefficient of water be the same in both phases, formula 18 is applicable to a salt with two univalent ions.

$$(f_{\pm}'/f_{\pm}'')^2 = m_{\text{Na}}'' \times m_{\text{Cl}}''/m_{\text{Na}}' \times m_{\text{Cl}}' \quad (18)$$

It is possible that formula 18 may prove useful in considerations of the state of equilibrium between the blood and the aqueous humour, discussed by Ridley¹² and by Davson, Duke-Elder, and Benham,¹³ who determined values for the ratios $r_{\text{Na}} = m_{\text{Na}}'/m_{\text{Na}}''$ and $r_{\text{Cl}} = m_{\text{Cl}}'/m_{\text{Cl}}''$, where L' represents plasma or serum and L'' represents the aqueous humour. If there be a state of equilibrium between the serum and the aqueous humour, then the function $1/\sqrt{r_{\text{Na}} r_{\text{Cl}}}$ should be equal to f_{\pm}'/f_{\pm}'' calculated by formula 18, for a system where the same serum is in equilibrium with a dialysate.

The analyses of sera and dialysates made by Hastings *et al.*¹⁴ are consistent with a value of $f_{\pm}'/f_{\pm}'' = 0.98$, and a value of 0.97 has been calculated from the analyses published by Marrack and Hewitt.¹⁵ The

¹⁰ Donnan, *Z. Elektrochem.*, 1911, 17, 572.

¹¹ Adair, *Science*, 1923, 58, 13.

¹² Ridley, *Brit. J. Exp. Path.*, 1930, 11, 217.

¹³ Davson, Duke-Elder, and Benham, *Biochem. J.*, 1936, 30, 773.

¹⁴ Hastings, Salvesen, Sendroy, and Van Slyke, *J. Gen. Physiol.*, 1927, 8, 701.

¹⁵ Marrack and Hewitt, *Biochem. J.*, 1927, 21, 1129.

function f_{\pm}'/f_{\pm}'' is not greatly changed by small differences in the protein content, and it is therefore permissible to regard the agreement between f_{\pm}'/f_{\pm}'' and the value 0.98 calculated for $1/\sqrt{r_{\text{Na}^+\text{Cl}}}$ as evidence for the existence of equilibrium between plasma and aqueous humour. A value of $1/\sqrt{r_{\text{Na}^+\text{Cl}}}$ 0.98 has been calculated from the distribution ratios for serum and ultrafiltrates given by Ingraham, Lombard and Visscher.¹⁶ Although the process of ultrafiltration was carried out at a pressure considerably higher than the observed osmotic pressure, their figures for the distribution ratios agree with the data of Hastings *et al.*¹⁴

In the above calculations of f_{\pm}'/f_{\pm}'' , and $1/\sqrt{r_{\text{Na}^+\text{Cl}}}$, based on the data of these authors,^{13, 14, 15, 16} no allowances were made for the hydration of the protein. If an allowance of 0.3 g. water per g. protein be made, the ratio f_{\pm}'/f_{\pm}'' is reduced from 0.98 to 0.955.

It is probable that proteins cause a real diminution in f_{\pm}' , which is masked partially by the effect of hydration. It is possible to prove that the effects on individual ions of the same sign are unequal, by the application of formula (14) to the experiments recorded by Adair and Adair.¹⁷ If the osmotic pressures be low and both of the ions be univalent, formula (14) can be replaced by the simple approximate formula (19).

$$\frac{m_i' f_i'}{m_k' f_k'} = \frac{m_i'' f_i''}{m_k'' f_k''} \quad (19)$$

Membrane Potentials and the Potentials of Individual Ions.

From the thermodynamical point of view, no criterion for the equilibrium of an individual ion across the membrane is necessary, because the possible variations in the state of the system are comprehended by equations (13) and (14), applicable to pairs of ions.

Under certain conditions it is however convenient to supplement formulæ (13) and (14) by (20), expressed in terms of the potentials of the ion S_i in both phases L' and L'' and the electrical potential difference ($E' - E''$) between these phases.

$$\mu_i' = \mu_i'' - n_i F(E' - E'') = \mu_i' - n_i F E \quad (20)$$

F = Faraday's equivalent in volt-coulombs. $E = E' - E''$. n_i the valence of the ion of species S_i is negative for anions.

This formula is comparable with an approximate formula (21) used by Loeb¹⁸ and by Adair and Adair¹⁹ in the correlation of membrane potentials and p_H values which are approximately equal to $-\log f_H m_H$.

$$p_H' = p_H'' - \frac{E}{0.05416} \times \frac{273}{273 + t} \quad (21)$$

It has been stated by Guggenheim²⁰ that the potential difference between two points in different media can never be measured. If, however, the solvent be the same in both phases and the solutions be ideal, the potential E can be calculated by formulæ (20) or (23). If the solvent be the same, and the solutions be not ideal, the potential can

¹⁶ Ingraham, Lombard, and Visscher, *J. Gen. Physiol.*, 1933, 16, 637.

¹⁷ Adair and Adair, *Biochem. J.*, 1934, 28, 1230. (Application of the theory of membrane equilibrium to iso-electric and iso-ionic points.)

¹⁸ Loeb, *Proteins and the Theory of Colloidal Behaviour*, New York, 1922.

¹⁹ Adair and Adair, *Biochem. J.*, 1934, 28, 199. (Membrane Potentials.)

²⁰ Guggenheim, *J. Physical Chem.*, 1929, 33, 842.

be estimated with the degree of accuracy obtainable in measurements with cells with liquid junctions, including p_H measurements, discussed in detail by Clark.²¹ A precise method for the measurement of membrane potentials with certain types of solutions containing proteins has been described by Adair and Adair.¹⁹ The observed potential, $E_{(obs.)}$ can be regarded as the sum of E , the potential in formula (20), $E_{(KCl|L)}$, the potential at the junction between the liquid L' and a saturated KCl-calomel electrode and $E_{(L''|KCl)}$, the potential at the junction between L'' and a second electrode. Since $E_{(L''|KCl)} = -E_{(KCl|L')}$

$$E_{(obs.)} = E_{(L'|KCl)} + E - E_{(L''|KCl)} \quad (22)$$

Although the liquid junction potentials may be of the order of 1.5 millivolts, in the types of solutions employed in biological experiments, it is reasonable to assume that if the compositions of the liquids L' and L'' be not very different, the difference between the liquid junction potentials in formula (22) is quite small. It is therefore convenient to adopt Clark's convention that a saturated solution of potassium chloride annuls the liquid junction potentials.

Approximate calculations of the effects of proteins on the activity coefficients of ions can be made,^{8, 17, 19} using the observed values of the potential and formula (23) which is the same as formula (20), expressed in terms of the molalities.

$$e^{h_i - h_1} m_i' f_i' / f_1' = e^{-n_i u} m_i'' f_i'' / f_1'' \quad (23)$$

The symbol u is an abbreviation of

$$u = EF/RT = E \text{ (in millivolts)} \times (1/23.535) \times (273/273 + t) \quad (24)$$

In solutions with low osmotic pressures, the terms e^{h_i} , f_1' and f_1'' can be disregarded.

Membrane Equilibrium in Systems where the Composition of One Phase is Constant.

In studies on proteins, it is often desirable to investigate solutions containing a mixture of inorganic electrolytes. If the protein solution L' be enclosed in a membrane permeable by all of the components except the protein, in equilibrium with the dialysate L'' of constant temperature, pressure and composition, the properties of the system are determined by one independent variable, the concentration of the protein in L' , even if the number of diffusible substances be unlimited. It has been shown^{22, 23} that the potential of the protein, or of the protein salt μ_{ps} is then correlated with the observed osmotic pressure p , and V , the volume of solution per mol of protein, by the formula

$$d\mu_{ps} = V dp.$$

Measurements on systems where L'' is of constant composition are required for the estimation of certain functions, f_{ps} and f_p , correlated with the activity of the protein^{22, 23} the osmotic²³ coefficient, g_{ps} , the functions f^* and ϕ , correlated with the distribution of a protein in a gravitational field,^{23, 24} the partial^{25, 26} pressures p_p due to protein.

²¹ Clark, *The Determination of Hydrogen Ions*, Baltimore, 1928.

²² Adair, *J. Amer. Chem. Soc.*, 1929, **51**, 696.

²³ Adair, *Trans. Faraday Soc.*, 1935, **31**, 98.

²⁴ Roche, Roche, Adair and Adair, *Biochem. J.*, 1935, **29**, 2576.

²⁵ Adair, *Proc. Roy. Soc. A.*, 1929, **126**, 16.

²⁶ Adair and Robinson, *Biochem. J.*, 1930, **24**, 1864.

ions and p_i due to the excess of diffusible ions inside the membrane, and the valence of the protein ions.^{19, 26}

The relationship between osmotic pressures, protein concentrations, molecular weights of haemoglobin^{8, 27} and serum proteins in systems where L' is constant and also the effects of proteins²⁶ on the activity coefficients of diffusible ions^{8, 17, 19, 26} have been described elsewhere. In the calculation of the activity coefficient of the protein, additional experiments may be required, in which the molality is kept constant and the salt concentration is varied.²³

The observed osmotic pressure p in a system of this type may be correlated with the osmotic pressures π' and π'' of the solutions L' and L'' , measured by membranes permeable by water, by applying formula 1 to a system with two membranes permeable by water and one membrane permeable by all the components in L'' .

$$p = P' - P'' = \pi'_{P'} - \pi''_{P''}.$$

$\pi'_{P'}$ = osmotic pressure of L' at the hydrostatic pressure P' .

$\pi''_{P''}$ = osmotic pressure of L'' at the hydrostatic pressure P'' .

Membrane Equilibrium in Ideal Solutions with Low Osmotic Pressures.

Donnan¹⁰ in 1911 developed a theory of membrane equilibrium in very dilute solutions. The importance of his theory has been emphasised in the work of Procter, Sørensen and Loeb.^{18, 28} A simple method for extending the theory to ideal systems with low osmotic pressures, including colloidal solutions in mixed solvents, has been suggested,^{8, 26} in which the composition of the solution L' is expressed in "corrected concentrations" in g. mols. per litre of the mixed solvent, calculated by formula (25).

$$[S]_0' = [S]_0 \times 100 / (100 - V_1 C) \quad . \quad . \quad . \quad (25)$$

$[S]_0'$ = corrected concentration of substance S in L' .

$[S]_0$ = observed concentration in mols per litre of solution.

C = g. colloid per 100 c.c. solution.

V_1 = volume occupied by 1 g. colloid, including water of hydration.

A relationship between the corrected concentration of a colloid S_p and the osmotic pressure in a mixed solvent containing the diffusible non-electrolytes S_1, S_2, S_3 in an ideal system has been obtained by applying formula (9),

$$N_p = N_1'(e^{h_1} - 1) + N_2'(e^{h_2} - 1) + N_3'(e^{h_3} - 1) \quad . \quad (26)$$

If the pressure $p = P' - P''$ be small, $e^{h_1} = 1 + h_1$,

$$N_p RT = p(N_1'v_1 + N_2'v_2 + N_3'v_3) = p(V - N_p v_p) \quad . \quad (27)$$

V = volume of solution containing N_p mols. of S_p .

The conditions for the equilibrium of diffusible ions have been stated below in terms of corrected concentrations for a system of the type described by Donnan.¹⁰ The solution L' is composed of water, a fully ionised sodium proteinate, $\text{Pr}(\text{Na})_n$, where n = the number of sodium

²⁷ Adair, *Proc. Camb. Phil. Soc. (Biol.)*, 1924, 1, 75.

²⁸ Lists of references are given by Bolam, *The Donnan Equilibrium*, London, 1932. See also¹⁹. Hober, *Physiological Reviews*, 1936, 16, 52, gives references to different types of membrane equilibria.

ions, and sodium chloride. Let $x = n \times [\text{Pr}]_e' =$ corrected equivalent concentration of $\text{Pr}(\text{Na})_n$, $y = [\text{Cl}]_e' = [\text{NaCl}]_e'$ (free) = corrected concentration of NaCl . $(x + y) = [\text{Na}]_e'$.

The solution L'' , separated from L' by a membrane permeable by water and salt, contains sodium chloride free from protein.

$$s = [\text{NaCl}]_e'' = [\text{NaCl}]_0'' = [\text{Na}]_0''.$$

In the absence of protein, the corrected concentration is equal to the observed concentration in mols. per litre of solution.

The condition for osmotic equilibrium is given by formula (28).

$$P = RT([\text{Pr}]_e' + [\text{Na}]_e' + [\text{Cl}]_e' - [\text{Na}]_e'' - [\text{Cl}]_e'') = RT([\text{Pr}]_e' + z) \quad (28)$$

$P = P' - P''$ and $z =$ excess of diffusible ions inside the membrane. $[\text{Na}]_e' = (x + y)$.

The condition for the equilibrium of ions is given by the formulæ (29), (30) and (31).

$$[\text{Na}]_e' \times [\text{Cl}]_e' = [\text{Na}]_e'' \times [\text{Cl}]_e'' \quad (29)$$

$$(x + y) \times x = s \times s \quad (30)$$

$$E = - (RT/2.303F) \log [\text{Na}]_e' / [\text{Na}]_e'' \quad (31)$$

In practice, it is convenient to supplement the equations by formulæ applicable to special problems. In some cases it is necessary to calculate the values of y required to maintain equilibrium when x and s must be kept approximately constant. Formulæ for the calculation of y and also x , s , z , and the distribution ratio $r = [\text{Na}]_e' / [\text{Na}]_e''$ are stated below.

$$x = \frac{s^2}{y} - y = s \left(r - \frac{1}{r} \right) = \sqrt{s^2 - 4zs} \quad (32)$$

$$y = \sqrt{s^2 + \frac{1}{4}x^2} - \frac{1}{2}x = s/r \quad (33)$$

$$s = \sqrt{(x + y)y} = yr = (x + y)/r \quad (34)$$

$$r = \frac{x + y}{s} = \frac{s}{y} = \sqrt{\frac{x + y}{y}} = \sqrt{1 + x/y} = \frac{x}{2s} + \sqrt{1 + x^2/4s^2} \quad (35)$$

$$z = x + 2y - 2s = 2\sqrt{s^2 + \frac{1}{4}x^2} - 2s \quad (36)$$

These formulæ apply to mixtures of univalent ions, if y denote the total corrected concentration of ions of the same sign as the protein and $(x + y)$ the total corrected concentration of ions of opposite sign, and s the total concentration of cations in L'' .

In systems where there is a mixture of univalent and bivalent ions, the calculations are less simple, and it is sometimes convenient to use approximate formulæ, supplemented by tables.¹⁹ If, for example, the sum of the concentrations of the ions in the dialysate multiplied by the squares of their valences is represented by the symbol J , the following formulæ can be applied to calculate the ion pressure difference $p_i = RTz$, and the valence of the protein, if the membrane potential be small.

$$m_p n_p = uJ \quad (37)$$

$$p_i = \frac{1}{2} u^2 RTJ \quad (38)$$

$$p_i = \frac{1}{2} RT(m_p n_p)^2 / J \quad (39)$$

m_p = corrected concentration of protein in mols. per litre of solvent. It may be noted that if E_m = membrane potential in millivolts at 0°C ,

then $p_i = 15.4 (E_m)^2 J$, in mm. mercury at 0°C. , and $n_p = 0.00425 MJ E_m / C_v$, where M = molecular weight of protein and C_v = g. per 100 c.c. solvent.

Dialysis.

The theory of membrane equilibrium may be applied to the process of dialysis, because the rate of removal of a diffusible impurity S_n from a colloidal solution L' , enclosed in a membrane surrounded by pure water is partly determined by the distribution ratio $r_n = [S_n]_c' / [S_n]_c''$

$$-d[S_n]_c' / dt = [S_n]_c' \left(\frac{1}{r_n} \right) k_n \quad (40)$$

t = time, k_n is a coefficient, directly proportional to the area of the membrane and the diffusion coefficient of S_n in the membrane, and inversely proportional to the volume of the solution L' and the thickness of the membrane. k_n is an undetermined function of the shape of the membrane, the rate of stirring and other factors. On the assumption that k_n is a constant, the reciprocal of the distribution ratio, given in Table I., column 3, is a measure of the rate of dialysis. The

TABLE I.

Molarity in L' .	Liquid Surrounding L' .	Dialysis Rate.	Volume of Dialysate.
Na 0.002	H ₂ O	0.0050	280.0
Na 0.004	H ₂ O	0.0040	270.0
Na 0.006	H ₂ O	0.0040	220.0
Ca 0.003	H ₂ O	0.0005	1800.0
Na 0.006	KCl 0.06	0.9500	1.05
Ca 0.003	KCl 0.06	0.9000	1.1

distribution ratio r_n is directly proportional to the volume of dialysate which would contain the same quantity of the substance S_n as is contained in one volume of the solution L' . These volumes are given in the fourth column of Table I. The calculations were made by assuming that a solution of hæmoglobin, approximately 0.002 molar, combined with sodium hydroxide or calcium hydroxide. The molarities of the bases combined are given in the first column. The concentrations of hydrogen and hydroxyl ions in a solution containing known amounts of protein and sodium hydroxide were calculated from titration curves.¹⁷ The distribution ratios were then calculated by formula (35), assuming that $y = [\text{OH}]_c'$ and $(x + y) = [\text{Na}]_c'$. Similar calculations were made for the calcium salt, using the formula $[\text{Ca}]_c' ([\text{OH}]_c')^2 = [\text{Ca}]_c'' ([\text{OH}]_c'')^2$. The figures in Table I. give a rough idea of the quantities of distilled water required for dialysis. In the case of a membrane containing 10 c.c. of protein solution, approximately 3 litres of water may be required to remove half the sodium, and approximately 18 litres may be required if the base be calcium. If the calcium salt be not completely ionised, the volume may be greatly increased. The most important point shown by the table is that the process of replacement of sodium or calcium by another ion, for example, potassium, takes place much more rapidly than the process of purification by distilled water. It will be seen that 10 c.c. of the potassium chloride solution may remove more sodium from the solution than 2 litres of distilled water. The effect of salts on the rate of removal of impurities is of importance in studies on systems where the composition of the dialysate is constant.²²

Summary.

The rigorous criteria for equilibrium across semipermeable membranes due to Gibbs and to Donnan and Guggenheim have been restated. Functions symbolised $[v_1]$ a mean volume, and $h_1 = (P' - P'')[v_1]/RT$ have been defined in order to simplify the statement of the exact formulæ in terms of molalities and pressures.

It has been shown that certain terms not usually included in approximate formulæ for membrane equilibrium may be of importance at high pressures, or in systems where large molecules can diffuse across the membrane.

The calculation of the ratio of the mean activity coefficients of the ions of a salt has been suggested as a criterion for equilibrium.

The theory of membrane equilibrium and osmotic pressures in ideal systems with low osmotic pressures has been discussed and applied to the process of dialysis.

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STRUCTURE IN RELATION TO LIVING BIOLOGICAL FUNCTIONS.

By J. H. SCHULMAN.

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It will be shown that it is possible to measure associations and interactions between large molecules in a quantitative manner, by the methods of surface potential and surface pressure. These associations are between the respective hydrophobic portion and polar groups of the molecules. They are not of true chemical nature since, on crystallisation from the equimolecular mixed solution, they usually separate out into their components, or if chemical complexes are formed they are extremely labile. Although labile in solution these complexes are extremely stable when in an orientated form at interfaces. These associations in solution are such that the biological and chemical functions of the components are completely changed.

The degree of association is very sensitive to small changes in the magnitude of the resolved electric moment of the associating polar group. This is effected by the position and magnitude of neighbouring polar groups or double bonds, salt concentration, p_H of the aqueous solution and temperature.

The nature of the two hydrophobic associating portions of the molecule also plays an important part in the stability of the complex; thus an insertion of a double bond into a suitable position in a saturated ring system or hydrocarbon chain can break down or increase the association. It will be shown that a grading of the reactivity of polar groups can be measured by the above-mentioned methods.

In natural systems where one would expect association between molecules to take place, such as in membranes, the molecules constituting these systems possess the most reactive dipoles (or polar groups suitably attached to a hydrophobic group) so far measured. The reactivity of

these molecules to association is very sensitive to all the conditions mentioned.

Biological substances which are active in very small concentrations appear to possess all the characteristics suitable to form associations with the various components in the serum, or living membranes. As a result of experiments in which interactions between comparative simple molecules were measured, it was considered feasible to measure the interaction of the chemical components from living membranes (*e.g.*, cholesterol, sphingo-myelin, cephalin and protein) in mixed monolayers on aqueous solutions, in similar proportions to those in which they exist in red cell membranes. Further, then to inject into the underlying solution, biologically active substances such as hæmolytic, agglutinating, or sensitising agents, and study the effects these substances have on these synthetic membranes made at an air liquid interface. These results were compared directly with the same systems working in solution, such as hæmolysis or agglutination of red cells.

While examining these systems a new phenomenon termed "film penetration" was discovered. If, for instance, under a monolayer of orientated molecules consisting of a large hydrophobic portion or "tail" and a polar group or "head," similar molecules be injected into the underlying solution, the following alteration in the surface potential and pressures of the film forming molecules may take place. If there is no association between the polar groups of the film-forming molecules and the injected molecules, no alteration in the film characteristics is noticed (even if the hydrophobic portions are soluble in one another).

1. If there is association between the polar groups, but none between the "tail" or hydrophobic groups, then an adsorption of the injected molecules on to the film molecules takes place, with a consequent change in surface potential, but no increase in surface pressure.

2. If there is association between both the head group and tail groups of the two respective molecules, then each polar group of the film-forming molecules anchors a polar group of the injected molecule. The hydrophobic portion of the injected molecule associates with the hydrophobic group or tail of the film-forming molecule and thus penetration of the monolayer takes place.

The number of molecules in the monolayer is thus suddenly doubled, the surface pressure consequently rises sharply.

Since the stability of such a mixed film of associating molecules is much greater than that of either of the two components, very large surface pressures are recorded on penetration (of the order 50 to 60 dynes/cm. change). The surface potential rises or falls to the value of that of the film composed of equimolecular mixture of the two respective molecules at their highest compression.

It will be shown that all those substances which only adsorb as in Case I. and change the surface potential, only agglutinate or sensitise red cells.

All those substances that penetrate monolayers (Case II.) of the substances that compose the Red Cell membrane, are hæmolytic.

Experimental.

Methods.—The methods of surface potential and surface pressure were used to determine interaction in mixed films. Since with the "injection" technique of adding active substances to the underlying solution,

the barrier system on the Langmuir trough could not be used, owing to the substances coming up to the surface on both sides of the barrier from the underlying solution, the ring method was used. This consisted of two rings attached to two chainomatic balances being placed on either side of the barrier, thus enabling the surface pressures of two films on the same aqueous solution to be compared under identical conditions. The chainomatic was so constructed that surface pressure differences of 60 dynes/cm. could be registered in a very short time interval.

Mixed Films.

Since the governing factors both in the mechanism of penetration, adsorption and stability of mixed films, are dipole interaction and hydrocarbon adhesion, mixed films of molecules containing varying dipoles attached to hydrophobic groups also varying in character were studied.

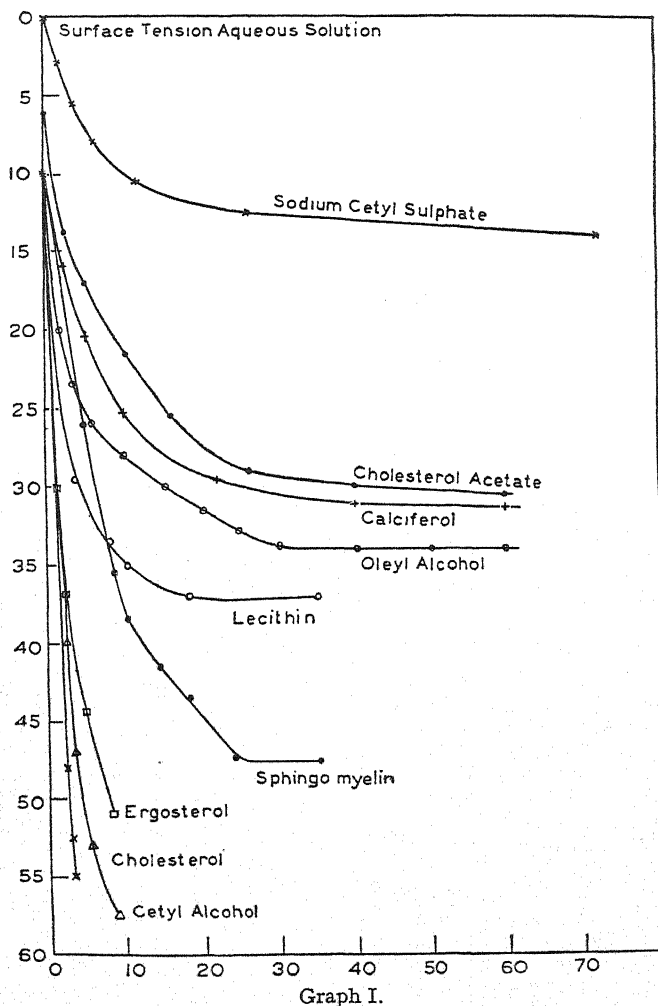
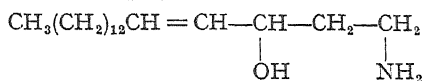
The adhering qualities of a hydrocarbon long chain are very considerably reduced by the presence of a double bond in the middle of the chain. Therefore a molecule with a weak interacting dipole attached to an olefine of the above description should only show very weak association. On compression of an equimolecular mixed film of oleic acid and cetyl alcohol on an aqueous solution of p_H 2, the association is so weak between the molecules that at a pressure where the oleic acid film usually collapses, the oleic acid is squeezed out of the surface leaving the alcohol molecules ultimately alone on the surface. The surface potential of the mixed film is identical to that of the mean of the surface potentials of each film at corresponding areas per molecule. If, on the other hand, two saturated long chains are now chosen a considerable condensing effect on the mean areas of the molecules of the two films is noticed, no separation of either component takes place on compression and there is a distortion effect of the mean of the two surface potentials from that of the calculated of + 23 mv.'s. If an ionised COO^- be now taken such as spreading the mixed film on a substrate of p_H 7.2, no separation of the oleic acid from the cetyl alcohol mixed film takes place, strong condensation of the area of the films and a distortion of the mean surface potential by - 30 mv.'s is noticed. With the saturated chains on p_H 7.2 the distortion is even greater being - 53 mv.'s. If one now moves the double bond to the α - β position as in *iso*-oleic acid, the dipole moment of COOH rises from 220 millidebyes to 450 millidebyes, this causes a very marked increase in the condensation and the stability of the long chain acid/alcohol mixed films on acid solutions of p_H 2 and the distortion effect (involving re-orientation of polar groups) on solutions of p_H 7.2 has been increased to - 73 mv.'s.

The association to the carboxyl or alcohol dipole of an ester dipole is very weak, since no distortion of the potentials is observed and on compression of the mixed film the ester molecule is ejected from the surface film.

Strong interaction is observed with amines. Such that on acid solutions of p_H 2 where the amine film is in the vapour expanded state, when mixed equimolecularly with a long chain COOH fatty acid in the liquid condensed state this results in a very strong and stable solid condensed film being formed. This film stands pressures very much greater than either of the two components alone (50-60 dynes). The surface potential distortion is + 140 mv.'s. The significance of the amine carboxyl dipole association, even in strong acid solution will be discussed again later in relation to the stability and formation of protein films.

An even more striking example of the stability of interacting dipoles is when one of the components is too soluble to form a monolayer on its own, but when in equimolecular mixture with an associating molecule forms extremely stable and insoluble films. Good examples of this are long chain sulphates, sphingosin and psychosin, combined with alcohol dipole or acid dipoles and soaps with an amine at p_H 9.5. It is again perhaps a significant fact that the most reactive dipoles are the amine alcohols

and strongly ionised acid groups activated by the near presence of a double bond, and that these groups are used by nature wherever association is to be expected, such as in membranes. Sphingo-myelin or cerebrin contains the active sphingosin polypole



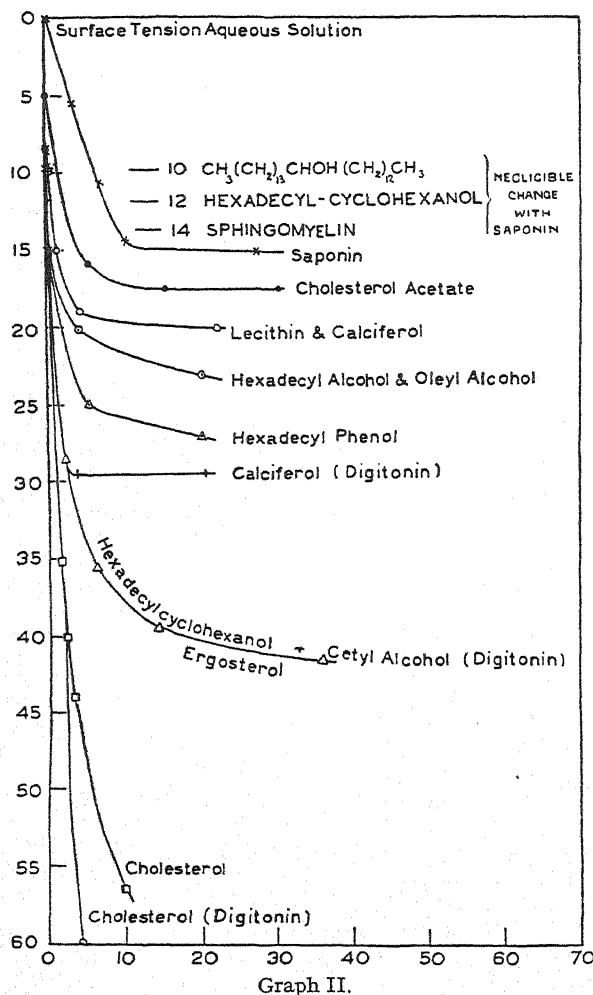
The sterols contain secondary alcohol dipoles activated by the near vicinity of a double bond. Proteins probably make full use of these associating dipoles and their sensitivity to environment, this will to some extent be shown experimentally later.

Penetration.

A very striking example of the effect of slight changes in the dipole, or structure of the hydrophobic group on association is given by the phenomenon of film penetration. If 1 mg. of sodium cetyl sulphate is injected

into 300 c.c. of solution of p_H 7.2 under a film of cholesterol, which has been compressed to 10 dynes/cm. (this value is the surface tension lowering of the free surface of the aqueous solution by the sodium cetyl sulphate alone), there is an immediate sharp rise in surface pressure of 50 dynes/cm. of the cholesterol film, the liquid film solidifies and the surface potential falls to that of the equimolecular mixed film value. In graph I. is shown the effect of changing the alcohol dipole in the cholesterol to that of an ester which has weak associating powers. Very reduced penetration is observed (about 18 dynes/cm. in 30 minutes).

Weakening the hydrophobic association of the two molecules by in-



insertion of double bonds into the ring system as in calciferol, has an equally large reducing effect on the penetration of such films by sodium cetyl sulphate. Another example of this is the effect on the penetration of films of cetyl alcohol by cetyl sulphate, this is of the same order as that of cholesterol. But the simple insertion of a double bond as in oleyl alcohol, radically reduces penetration.

It is interesting that in the experiments showing weak penetration, that if the films be compressed to the values which they ultimately attain after penetration, no penetration of these films now takes place. This is equivalent to weak associating mixed films where one component can be squeezed

from the surface. On the other hand where strong association is observed, previous compression of the film does not stop the penetrating molecules.

In order to prove further that dipole association is the primary factor in penetration a series of experiments were carried out with substances which are known to give associations in solution, such as saponin-cholesterol complexes. It will be seen that the factors controlling complex formation in solution are identical with those acting in the monolayers.

But whereas the complex formation is extremely difficult to measure in solution, it is comparatively easy to do so in a quantitative manner in film reactions. Saponin is very much more specific in its penetrating properties than sodium cetyl sulphate and only penetrates films of cholesterol and ergosterol (Graph II.). As with the cetyl sulphate the association is immediately broken down by the insertion of double bonds into the sterol ring system as in calciferol, or changing from the strong alcohol dipole to a weak associating one as the ester in cholesterol acetate. On the other hand digitonin contains a more reactive dipole, than saponin instantly penetrating a cholesterol film, forcing the surface pressure to values of 60 dynes/cm. in 2 minutes and solidifying the liquid film. It also to some extent penetrates straight chain alcohols such as cetyl alcohol and hexadecyl-cyclo-hexanol films of which saponin won't penetrate. Digitonin shows the same sensitivity to variations in the polarity of the molecules, in penetration as saponin.

Such substances as sodium oleate, sphingosin, psychosin, taurocholic acid penetrate very actively films such as long chain acids, alcohols, amines, in the same manner as described by these two examples (*e.g.*, Lowering or raising the surface potential to the equimolecular mixed film values at their greatest compressions, and markedly raising the surface pressure of the film forming substance). If the penetrating substance itself lowers the surface tension in a marked manner (sodium oleate) displacement of the mixed film can follow in time. This is probably due to some form of surface emulsification and usually takes about 2 hours to complete at concentrations of 1 mg./300 c.c. for sodium oleate on a tripalmitin film at p_H 7.2.

Measurement of Complexes in Solution.

Since all penetrating substances are hæmolytic the inhibition of hæmolysis and in some cases increase in lytic activity is a measure of the interaction of associating molecules. Sodium cetyl sulphate which is very strongly hæmolytic loses all its lytic activity when combined in equimolecular proportions with cholesterol. It maintains its lytic activity when dipole association is weakened, as when it is combined with cholesterol acetate, or with calciferol when the hydrophobic association is weakened. Saponin acts, as is well known, in a similar manner. Long chain alcohols which are too insoluble to be lytic on their own, but when mixed equimolecularly with sodium cetyl sulphate immediately become very lytic and dispersed in aqueous solution. The long chain alcohols penetrate and disperse protein films in a marked manner, which as will be explained later may account for their hæmolytic activity. The carboxyl group as in palmitic acid, is not sufficiently reactive with the OH group in the cholesterol and the complex is not sufficient to stop the hæmolytic activity of the carboxyl fatty acid.

Another method of measuring the associating activity of sodium cetyl sulphate is the inhibition of the precipitation of the silver salt, when for example cholesterol has been added equimolecularly to the sodium cetyl sulphate.

Lipo-Protein Mixed Films.

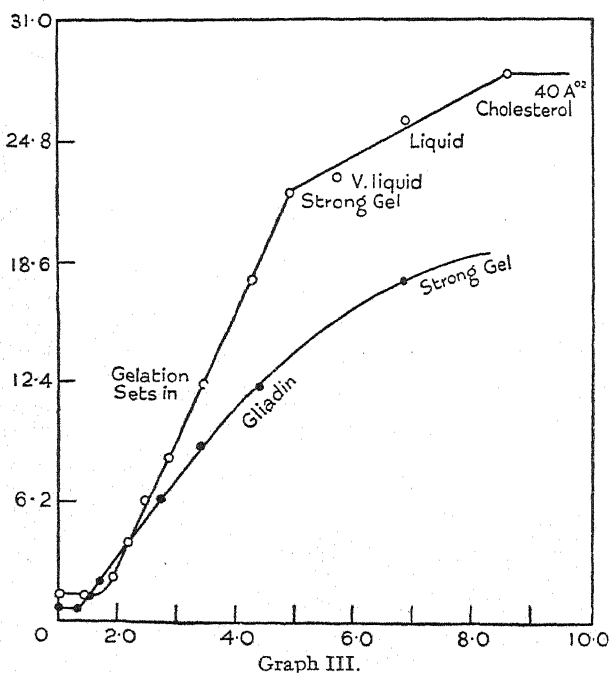
Water soluble proteins when spread at air/water interfaces form insoluble mono-layers of gel like structure. From the work of Gorter¹ on ferment films, who showed that this process does not impair the activity of the ferment, the protein can be considered as not being denatured.

As the protein unit spreads out on to the surface polar groups will separate out from the non-polar portion and stretch the unit on the surface. Since this unit is extremely polar it should be drawn into the solution in which it is very soluble. It is suggested that it stays there, because, first,

¹ *Proc. Roy. Soc.*, 1936, 155.

the polar groups consist chiefly of free amines, carboxyls, ketonic and imido dipoles; the amino and carboxyl groups are situated mainly on the ends of the side chains, the rest in the main chain or backbone of the unit. It has been shown earlier in this paper that the ionised amine dipole forms a very strong association with the carboxyl dipole even on $N/100$ acid substrates. It is therefore suggested that these dipoles will interact and associate *inter-molecularly* as soon as the dipoles are spread on the surface; this enables the units to link across into a wide network and remain on the surface. Since the unit is so large it can now no longer go into solution, and the network gives it its gel-like structure.

The Keto-imido groups will chiefly inter-link *intra* molecularly thus favouring a α -keratin form, as suggested by Fossbinder,² in the first open network. On compression of this open network together more reactive polar groups come into contact with one another, probably all the types already mentioned and others specific to the various proteins. These



associate and give multiple point contacts, the gel structure becomes much stronger and the network is now in three dimension. Detailed positions of an ideal protein molecules during various stages of compression according to the weight per sq. cm. of the film have been given by Hughes,³ but without the dipole association factor.

If capillary active substances containing polar groups which can associate with the protein polar

groups be injected into the solution under such a film, the breakdown of this network can be visualised. Thus stronger associating dipoles will break the inter-unit linkages and disperse the protein units into solution. This phenomenon occurs within three minutes with substances such as sodium oleate, psychosin, cetyl sulphate, taurocholic acid, etc., in concentrations of 10^{-5} per cent. Saponin on the other hand adsorbs strongly on to protein films strengthening the gel-like structure. It reduces the surface potential of a gliadin film at p_H 7.2 from 330 — 230 mv.'s. It will be shown later that the protein units can be artificially inter-linked with tannin so that the units cannot be broken down and only penetration of the protein film takes place.

Gliadin possesses the valuable property of being soluble in 75 per cent.

² J. Franklin Inst., 1933, 578.

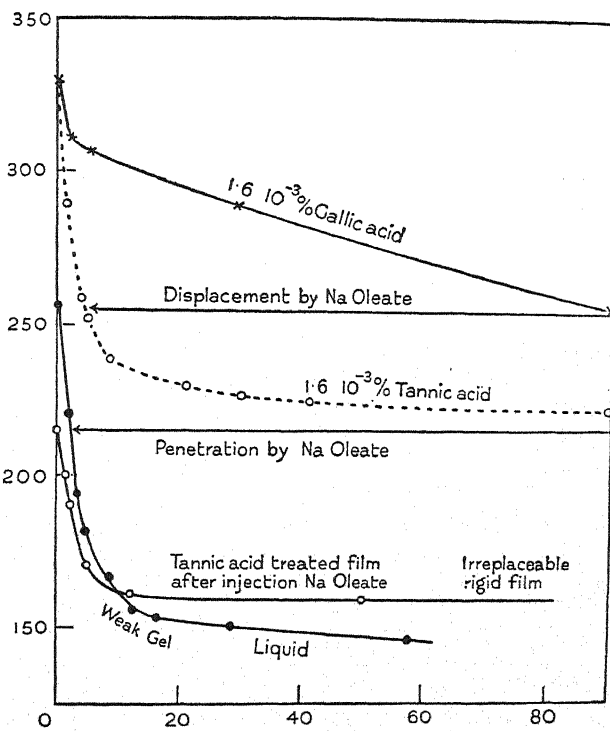
³ Proc. Roy. Soc. A, 1932, 137.

alcohol, thus permitting cholesterol and sphingomyelin and protein mixtures to be spread in monolayers. Graph III. shows a 20 per cent. cholesterol and 80 per cent. gliadin mixed film; on compression of this mixed film on p_H 7.2 strong gel formation takes place up to pressures of 22 dynes/cm. On increasing pressure above this point complete liquefaction of the film takes place. The film then possesses all characteristics of a cholesterol film, as regards area, surface potential and "punkt structure." The protein has disappeared, no striations forming on strong compression. On re-expansion of this liquid film strong regelation takes place at the same point. The protein has re-appeared and reforms a mixed monolayer. It could be suggested that the active alcohol dipole of the cholesterol anchors a polar group of the protein unit, which enables the compressed film to behave as a double layer film, on re-expansion a monolayer can be reformed.

The strength of the gelation of the film being a function of the number of associating polar groups amongst the protein units, it is interesting in this connection that intermixing of cholesterol encourages the gel formation of the protein film on p_H 's more alkaline than 6.8, whilst on acid p_H 's of 6.2 or less no gelation of the film over the whole range of compression takes place. (Iso-electric of gliadin p_H 6.5.) Salts also considerably affect the gelation of the mixed film, making the films more liquid, or peptising them.

Triolein in the same proportions (*i.e.*, 20 per cent.) completely liquefies the protein film over the whole range of compression and p_H , but curiously does not contribute any change to the gliadin surface potential.

Tripalmitin (20 per cent.) likewise liquefies the gliadin films but not to the same extent, as gelation takes place on strong compression. It, likewise, although possessing a very high surface potential (700 mv.) does not contribute to the gliadin surface potential. (Slight traces of free fatty acid would have strong effects on the gelation of the film.) Sphingomyelin possessing very active polar groups encourages the gelation of the gliadin film and contributes to the surface potential. It was possible to make a mixed monolayer of sphingomeglin, cholesterol and gliadin in ratio 1:1:4, which possessed characteristics similar to the cholesterol



Graph IV.

gliadin mixed film alone. Certain analogies may be drawn from the manner in which the components of membranes as found in living systems, contain strong associating groups, thus forming remarkably stable mixed films on aqueous solutions. Slight alterations in environment change these associating conditions, so that one could imagine this to have radical effects on molecules or ions diffusing through membranes as in living systems.

The varying degree of reactivity of different polar groups and hydrophobic groups in their associating power might likewise play an important part in many biological functions.

Adsorption.

Molecules in a monolayer which can anchor through their dipole association molecules from the underlying solution, which have no hydrophobic adhesion to one another, do not penetrate monolayers, but only adsorb on to them. Thus no increase in the surface pressure of the monolayer is noticed but only changes in the surface potential. The rate of adsorption is dependent on the degree of association between the respective dipoles or ions, on the number and spacing of the associating dipoles per molecule of the adsorbing component and perhaps on potential barriers beneath the film. Gallic acid (Graph IV.) at a concentration of $1.6 \cdot 10^{-3}$ per cent. takes three hours to adsorb on to a gliadin monolayer at p_H 7.2 while tannic acid with 10 galloyl units in one molecule takes 10 minutes at identical concentration. It is interesting in this connection that the gallic acid treated proteins are readily dispersed by fatty acids injected into the underlying solution, but the tannated protein film is not dispersible. The protein units have been interlinked in a non-dispersible network by the multiple point contacts of the large tannic acid molecules. Only penetration by the fatty acid molecule takes place into such films.

Dyes such as Janus green adsorb strongly on to gliadin films increasing the surface potential 160 mv.'s at p_H 7.2; in strong concentrations they increase the surface pressure of protein films, behaving like weak penetrating agents.

Possible Mechanisms for Hæmolysis and Agglutination.

If one considers the outer membrane of a red cell to be a mixed lipoprotein monolayer composed of 20 per cent. lipid (cholesterol, sphingomyelin, and kephalin) and 80 per cent. protein, certain analogies may be drawn from the action of hæmolytic, sensitising and agglutinating agents on mixed monolayers composed of these lipoids and proteins. The analogies are striking, since all hæmolytic agents such as, fatty acids ($-\text{COO Na}$ and $-\text{SO}_3 \text{Na}$) psychosin, taurocholic acid, saponin, digitonin, penetrate cholesterol or sphingo-meglin films and disperse protein films. Saponin being very specific in its penetration, will only penetrate cholesterol films, and adsorb on and penetrate protein films. Taurocholic acid also shows anomalies of this description.

Therefore penetration of cholesterol by saponin is prevented by compression of a mixed cholesterol, gliadin film to the pressures where the protein is underneath the cholesterol in form of a double layer. This double film on the other hand is immediately penetrated by the fatty acids. Substances such as pelargonic acid which owing to its small non-polar portion penetrates lipid films very slowly—likewise only hæmolyses very slowly.

The mechanism of penetration has been described as the specific anchoring by the polar group of the film forming substance of the polar group of injected substance, this anchoring enabling the hydrophobic

portion of the injected molecule to penetrate the monolayer if there is adhesion between the two respective non-polar portions.

On the other hand all substances which only anchor with their polar groups on to protein films and thus adsorb and are unable to penetrate lipid or protein films, only agglutinate red cells. Such substances are tannins or silicic acid which reduce the adhesion of the film to the aqueous solution.

Dyes which primarily adsorb and in strong concentrations penetrate protein films act as sensitisers.

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PROTEIN-FILMS.

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University of Ghent (Belgium).*

Received 22nd March, 1937.

Films of proteins, spread out on a water surface have special properties which deserve careful consideration. The two surfaces of such a film must be distinguished: the upper surface in contact with the air, which contains all the non-polar groups of the molecule and the lower, in contact with the water, which consists of the polar heads of the protein molecule.

This conception of a duplex film accords with Langmuir's theoretical explanation of Adam's films of myristic acid at different temperature; it holds good for proteins as well.

Very little is known of the upper surface of a duplex film of protein, and all our observations apply to changes in the film produced by some modifications of the polar groups. It is obvious that in a monomolecular protein-film the molecules are orientated. A simple calculation shows that this orientation differs from that of a protein in a solution, the thickness of a film of proteins is 10 Å. only, whereas according to Svedberg the radius of a globular molecule of the same protein is 22.5 Å. This difference must be ascribed to an unfolding of the globular molecule. The resulting flat platelet has the same surface as the globule from which it is derived.

It is a subject of controversy whether this process of unfolding is accompanied by a *denaturation*. Since a molecule of a spreading substance must consist of a soluble and an insoluble part, it is possible to predict that a soluble protein has travelled part of the way to denaturation. It has not, however, reached the end-point.

Experiment shows that pepsin and trypsin can be recovered from a water surface without having lost more than 20 per cent. of their activity. Neurath has proved that heat-denatured ovalbumin does not spread, and we have found that the addition of a trace of pepsin can restore the original spreading tendency.

A monomolecular film of protein influences in a remarkable way the potential difference which can be observed between the water in the tray

and the air above which is made conductive by a radio-active preparation. This potential jump is of the order of 300-450 millivolts. Its measurement over the whole surface of the film, permits a control of its homogeneity. Differences in the p_H of the water strongly influence the size of this potential difference.

Proteins exhibit important differences in their tendency to spread ;

with few exceptions they can all be induced to form a monolayer, but, on the other hand, very rarely does any protein form a monomolecular film under all experimental conditions.

We consider first the factors which counteract the spreading

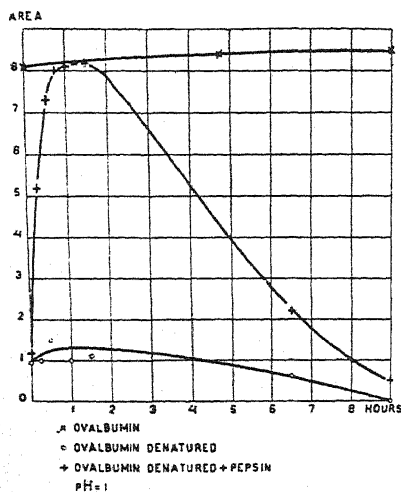
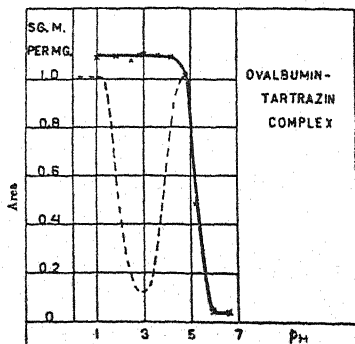


FIG. 1.—In the lower curve ovalbumin has lost its spreading tendency and does not recover it spontaneously. In the upper curve the spreading of ovalbumin is shown. The middle curve gives the spreading of denatured ovalbumin to which pepsin (1/50) had been added. The tendency to spread comes back completely in ± 1 hour and disappears again owing to the action of the pepsin.

tendency. One of the most important is the ionisation of the NH_3^+ and COO^- groups. Everything which prevents this ionisation increases the spreading tendency. This can be shown in different ways :—

(1) On adding electrolytes in sufficient amount to the water in the presence of a protein such as ovalbumin (which has a large number of both kinds of ionisable groups), spreading of the protein occurs almost immediately, and reaches completion at a p_H at which there is no spread-

FIG. 2.—The area in square meters is plotted against the p_H of the solutions in the tray. The solutions are prepared, between p_H 1.0 and 3.6, as dilutions of hydrochloric acid ; between 3.6 and 5.6 as acetate-acetic acid buffer solutions (1/300 M), and above 5.6 the veronal buffer solution of Michaelis in the same strength. The dotted line is the spreading of ovalbumin measured after two minutes, whereas the straight line gives the spreading of the tartrazin-ovalbumin-complex.



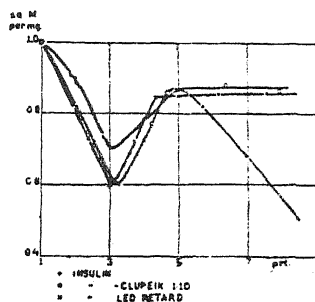
ing at all in the absence of electrolytes. Positive ions have an effect on the alkaline side of the iso-electric point and negative ions on the acid side. A valency rule can be observed. Bivalent ions have a more pronounced effect than univalent and trivalent ions are still more active ; a lyotropic series can also be noted.

(2) Complex proteins are obtained by the addition of bivalent acids or amines which are attracted to the NH_3^+ or COO^- groups. For example

Fig. 2 shows that by the addition of tartrazin* to ovalbumin the protein ovalbumin is transformed into a substance which behaves as a (fatty) acid. The influence of free NH_3^+ groups is no longer observable. Again, comparing insulin and the insulin-clupein complex (Fig. 3), the spreading tendency is increased on the alkaline side by the disappearance of the free COO^- groups. The pepsin-spermidin-complex (Fig. 4)

FIG. 3.—The area of the spreading of insulin, measured after two minutes is plotted against the p_H of the solutions in the tray; + insulin itself; \times the commercial product of the clupein-ovalbumin-complex, prepared by Dr. Maaskant in my laboratory.

The difference between the insulin itself and the two complexes consists in increased spreading tendency on the alkaline side of the iso-electric point, owing to the addition of a "polyamine" to the COO^- groups of the ovalbumin. A slight influence on the acid side is also seen.



shows how the replacement of the COO^- groups of pepsin¹ increases the spreading tendency on the alkaline side of the iso-electric point, but decreases on the acid side, owing to the addition of more NH_3 groups to the few (5) which exist in pepsin itself. (The same phenomenon can be seen in the insulin-clupein-complex, Fig. 3.)

Intermediate products, moreover, can be prepared, in which a smaller amount of the acid or alkaline substance is fixed to the protein, and spreading is promoted less than by the saturated product.

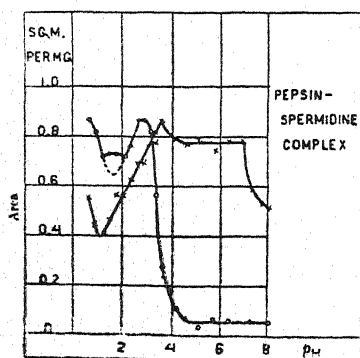


FIG. 4.—The size of the protein-molecule in square meters per mgr. plotted against the p_H of the solution in the tray. Measurements are made after 1 or 2 minutes; O pepsin itself; \times the pepsin-spermidin-complex.

The influence of this addition of a polyamine (spermidin) to the COO^- groups is seen in the increased spreading tendency on the alkaline side of the iso-electric point. The lower minimum on the acid side and the displacement of the iso-electric point to the alkaline side is explained by the greater number of NH_2 in the complex molecule, as compared to pepsin itself.

(3) The results on the artificially prepared complex-proteins indicate that the properties of the natural proteins also must differ according to their composition. The simple proteins, such as clupein, do not spread, because the "upper" surface of a film of this protein contains too many NH_3 polar groups and is therefore too soluble.

Other proteins (e.g. *myosin*, *fibrinogen* and also heat-denatured *ovalbumin*), do not spread because the lower surface contains too few free

COO^-

* Tartrazin is: $\text{SO}_3^- \dots \dots \text{SO}_3^-$.

¹ E. Gorter and L. Maaskant, *Proc. Kon. Akad. v. Wetenschappen*, 1937. 40, 71.

polar groups; for if these proteins are split into somewhat smaller particles, by which more COO^- groups and NH_3 groups are made free by traces of a proteolytic enzyme, the product has a normal spreading tendency.

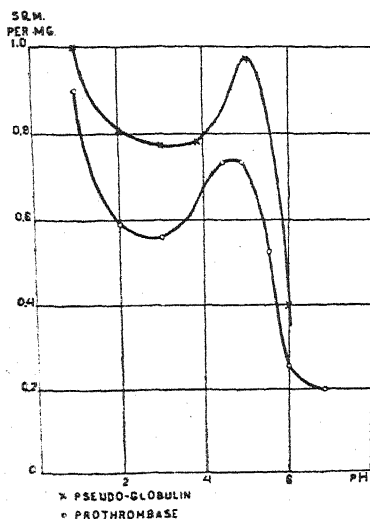


FIG. 5.—The area in square meters per milligram is plotted against the p_H of the fluid in the tray, \times pseudo-globulin, \circ a euglobulin such as prothrombase.

These results seem to indicate that the majority of the NH_3 groups are not free; so much so that their ionisation is prevented.

When the area of spread is plotted against the p_H several proteins of Fig. 5 (e.g. *pseudo globulin* and *prothrombase*) give curves characteristic of complex proteins, rather than curves similar to the dotted curves of Fig. 2 (ovalbumin). They behave as if part of their NH_3 groups are no longer free.

In almost every instance when there is a low spreading tendency, whether due to the properties of the protein itself or to those of the solution, *time* has a considerable influence; so much so, that after some hours complete spreading occurs under conditions which in a few minutes would lead only to feeble spreading. Having ultimately in mind an application to biological processes, rapid changes seem to me more important than slower ones; for example, when considering the physical changes produced in fibrinogen by the addition of prothrombase or in myosin by the addition

of proteolytic enzyme as indicated by the spreading method.

In connection with the possible application of these studies of proteins on biological problems, I desire to draw attention to the differences between the electrolyte contents of tissues and of body fluids respectively. It is obvious that proteins in fluids such as blood plasma must be capable of remaining in solution. This could not be effected by maintaining the same osmotic pressure with potassium ions, which would give to all proteins, the iso-electric point of which is lower than p_H 7.3, a strong tendency to spread. Sodium is used therefore for body fluids and potassium for the building-up of tissues, in which proteins need no longer be so completely soluble as in fluids.

Other examples are the high magnesium content of muscular tissue (and the presence of glutathion in tissues only), which gives to the proteins a strong spreading tendency, incompatible with protein-solubility in fluids. The table shows the electrolyte content of plasma and

	Ions in Tissues in Milliequiv./l. Muscle Water.	Ions in Body Fluids in Milliequiv./l. Serum Water.	Ions Promot- ing the Spreading of Proteins, Milliequiv./l. Showing Equal Effects.
Na . . .	48.0	154.0	160.0
K . . .	112.5	5.3	80.0
Ca . . .	5.2	5.1	4.0
Mg . . .	23.9	2.8	4.0
Glutathion	1	nil	1

muscular tissue after Peters and Van Slijke and the amounts of electrolytes which give a spreading tendency to proteins. There is rough agreement between the two series of figures.

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THE STRUCTURE OF PROTEIN MONOLAYERS.

By JOSEPH S. MITCHELL.*

Received 1st March, 1937.

One of the most important problems in the study of protein monolayers is the correlation of the macroscopic properties with the chemical structure and molecular configuration. An exact structural knowledge is essential, not only for the application of the technique of monolayers to the quantitative investigation of changes in proteins which are difficult to study by the older methods (for example, photochemical processes), but also because evidence is accumulating that protein monolayers are a fundamental unit in the submicroscopic architecture of living cells.

In this paper, the properties of monolayers of three proteins—a wheat gliadin, zein and insulin—whose products of hydrolysis are almost completely known, are examined at an air-water interface by the method of surface pressures, supplemented by observations of the phase boundary potentials and dark ground ultramicroscopy. An attempt is then made to elucidate the structure of the monolayers by interpretation of the observed properties in terms of the analytical data with the aid of the X-ray crystallographic measurements of interatomic and intermolecular distances, and the results of experiments on monolayers of simple compounds. The validity of the Fischer-Hofmeister peptide theory of protein structure is assumed throughout the discussion. This method of approach was first applied to proteins by Hughes and Rideal;¹ its value has been demonstrated and its reliability confirmed in the cases of a number of relatively complex organic compounds of much lower molecular weight than proteins, for example, the sterols,² stearic anilide,³ haemin,⁴ and the maleic anhydride compound of β -elaeosterin.⁵

The specimens of protein used were all of a very high degree of purity. The specimen of wheat gliadin was obtained from Dr. E. A. Fisher; its water content was determined by drying in air at 110° C. until the weight became constant, and was found to be 9.9 per cent. The zein was prepared by Dr. R. Gortner; its water content was 5.4 per cent. Two specimens of crystalline insulin were used; one (specimen J) prepared by Dr. H. Jensen, had a physiological activity of 26.3 units per mgm., and the other (specimen H) prepared by Dr. H. C. Hagedorn had a physiological activity of 23.7 units per mgm.

* Beit Memorial Research Fellow.

¹ Hughes and Rideal, *Proc. Roy. Soc., A*, 1932, **137**, 62.

² Adam, Askew, and Danielli, *Biochem. J.*, 1935, **29**, 1786.

³ Mitchell, *Proc. Roy. Soc., A*, 1936, **155**, 696.

⁴ Hughes, *Trans. Faraday Soc.*, 1933, **29**, 211.

⁵ Gee and Rideal, *Proc. Roy. Soc., A*, 1935, **153**, 116 and 129.

The Preparation of Protein Monolayers.

The essential requirement for the quantitative investigation of proteins in the boundary state is a reliable method of preparation of monolayers whose physical properties are reproducible and whose surface density is accurately known. It is evident that Langmuir's method is inapplicable and the results obtained by the surface concentration method⁶ are unsatisfactory.¹ The requirements appear to be fulfilled by the method introduced by Hughes and Rideal,¹ which consists in weighing a particle of the solid protein on to the surface of the substrate by means of a Nernst quartz fibre microbalance.^{7, 8}

TABLE I.

Concentration of Spreading Solution, gms. per 100 c.c.	γ_{lim} gms. per sq. cm. $\times 10^{-7}$.
0.979	1.04
0.101	0.55
0.0107	0.35
0.0078	0.35
0.0010	0.35

Monolayers with significantly different properties are obtained by the more convenient method of Gorter and Grendel⁸ and the magnitude of the discrepancy between the results given by this method and by that of Hughes and Rideal has been one of the outstanding difficulties in the quantitative examination of protein monolayers. It has been found that the properties of the monolayers prepared by spreading from solution vary with the concentration of the protein solution used, and attain limiting values with very dilute (0.01-0.001 per cent.) solutions. In the case of gliadin, the monolayers obtained by spreading from solutions of concentration 0.01 per cent. w./v. are almost identical with those spread from the solid by the method of Hughes and Rideal. Even with the dilute solutions, measurements of the phase boundary potentials have shown that after spreading, an interval varying from one to thirty-six hours is required to allow the attainment of apparent equilibrium in the film before observations are made.⁹ In Table I. and Fig. 1 is shown the variation of "limiting density" γ_{lim} , i.e., the extrapolated density for the appearance of measurable surface pressure, with the concentration of the spreading solution for the case of gliadin. In all the experiments the solvent for the protein was 70 per cent. v./v. aqueous ethyl alcohol and the substrate was N/100 sulphuric acid. The surface dynamometer was sensitive to 0.1 dyne per cm. The observations were made at room temperature (17°-21° C.) after an interval varying from one to fifteen hours and the value given for each concentration is the mean of at least

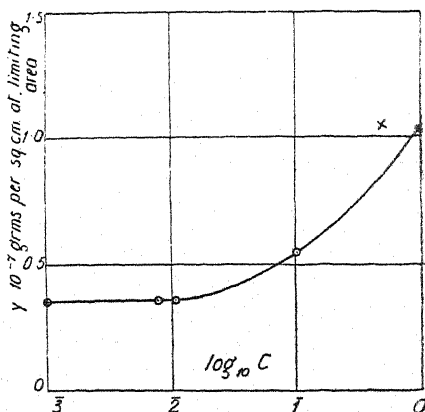


FIG. 1.—Variation of limiting density with concentration of spreading solution, for monolayers of gliadin on N/100 sulphuric acid (17°-21° C.).

⊙ ⊙ Present investigation.

× Gorter and Grendel⁸ ϕ_{H} .

⁶ Du Nouy, *Surface Equilibria of Biological and Organic Colloids*, 1929; Hercik, *Kolloidz.*, 1931, 56, 2.

⁷ Fosbinder and Lessig, *J. Franklin Inst.*, 1933, 215, 579.

⁸ Gorter and Grendel, *K. Akad. V. Wetensch. Amst.*, 1926, 29, 1262; *Trans. Faraday Soc.*, 1926, 22, 477.

⁹ Gorter and Philippi, *Kon. Akad. Wet. Amsterdam Proc.*, 1934, 37, 788.

four determinations. The concentration C of the spreading solution is given in grams of dried protein per 100 c.c. of solution and the "limiting density" γ_{lim} also refers to the mass of dried protein per square centimetre of the monolayer. It is evident from the experimental data that the limiting value has been reached for spreading solutions of concentration 0.01 per cent. w./v. and that this value ($\gamma_{\text{lim}} = 0.35 \times 10^{-7}$ gms. per sq. cm.) is very close to that obtained by Hughes and Rideal (0.36×10^{-7} gms. per sq. cm.). In the technique introduced by Gorter, the protein monolayers are usually spread ⁹ from 0.5 per cent. solutions, so that in at least some cases it is probable that the limiting properties are not attained. It is of great interest that the value for gliadin at $p_H 1$ given by Gorter and Grendel ⁸ lies close to the experimental curve (Fig. 1) for the variation of limiting density with concentration of the spreading solution; presumably at $p_H 2$ the density obtained by Gorter and Grendel's method would have a slightly higher value than at $p_H 1$. Probably the observed variation of the properties of the monolayers with the concentration of the protein solution must be attributed to the formation of micellar aggregates at the higher concentrations. However it is clear that essentially the same results are obtainable both by the method of Hughes and Rideal and by the method of Gorter and Grendel, modified by the employment of very dilute (0.01 per cent. w./v.) spreading solutions of the proteins and the introduction of prolonged time intervals (one to thirty-six hours) before observation. Throughout this work the monolayers examined were prepared by this modification of the technique of Gorter and Grendel. The volume of the protein solution dropped on to the surface of the substrate is measured by means of the "Agla" micrometer syringe. The completion of the spreading has been confirmed by measurements of the phase boundary potentials.

The solvent used for the gliadin and zein was aqueous ethyl alcohol of concentrations varying from 60 to 80 per cent. v./v.; the insulin was dissolved in $N/100$ sulphuric acid.

The results described refer to monolayers of proteins spread on $N/100$ sulphuric acid at room temperature (16.5°C. to 21.5°C.). The variation with p_H of the mechanical and electrical properties has been examined in considerable detail by Gorter,¹⁰ Hughes and Rideal,¹ Schulman and Rideal,¹¹ and Philippi,¹² and it is evident that in the correlation of the macroscopic properties with the chemical structure, the p_H of the substrate is of negligible importance, provided of course that the data on which the calculations are based refer to the p_H at which the measurements on the proteins were made. It is of advantage in comparing the mean properties of the repeating unit ($\text{CO}-\text{NH}-\text{CHR}$) in different proteins to utilise measurements at a given standard p_H (such as 2) considerably removed from the iso-electric points; further, the selection of a standard p_H outside the Svedberg stability ranges for micelles in bulk solution may minimise the influence of the length of the polypeptide chain.

The Properties of the Protein Monolayers.

The compressibility curves of monolayers of the gliadin, zein and insulin (specimens H and J) are shown in Fig. 2, where the surface pressure, F , in dynes per cm. is plotted against the surface density, γ , of protein in gms. per sq. cm. Each curve is the mean of at least four almost coincident curves. The values of γ refer to dried protein in the case of gliadin and zein, but to the crystalline protein in the case of insulin. The

¹⁰ Gorter, van Ormondt and Dom, *Konin. Akad. v. Wetensch. Amsterdam*, 1932, **35**, 838.

¹¹ Schulman and Rideal, *Biochem. J.*, 1933, **27**, 1581.

¹² Philippi, *On the Nature of Proteins*, Thesis, Amsterdam, 1936; Rideal, *Proc. Roy. Soc., A*, 1936, **155**, 684.

approximate mean thickness, δ , of the monolayers is calculated on the assumption that the density of the protein at the interface is 1.33 for gliadin and zein, and 1.31 for insulin.¹³ It is further assumed that the whole of the protein spread remains at the interface. All the curves are of similar type, and consist of three regions:—

1. A region over which the surface pressure is not measurable, *i.e.*, is less than 0.1 dynes/cm. extending from $\gamma = 0$ to the limiting area. This may correspond to the region of surface vapour pressure.

2. A "low pressure region," of high compressibility, extending from the limiting area to a surface pressure of the order of 1.2 dynes/cm. In the case of the proteins examined the film is liquid with negligible elasticity and rigidity.

3. A "high pressure region" of low compressibility extending to the collapse point.

In the proteins studied, the inflexion point between regions 2 and 3 corresponds to the appearance of elasticity in the film and probably also to the onset of gelation. However, films of insulin—specimen H—are apparently liquid at all pressures, although those of insulin—specimen J—become rigid gels immediately before collapse. The inflexion point is sharp only when the film is completely spread. With stable films, there is negligible hysteresis in the high pressure region except near the collapse point, but metastable films are easily produced by rapid compression.

The limiting area and the limiting area of the high pressure region extrapolated to zero pressure are the two most characteristic mechanical properties of the monolayers. Neither are significantly influenced by the interval between complete spreading and compression, although the compressibility of the high pressure region decreases

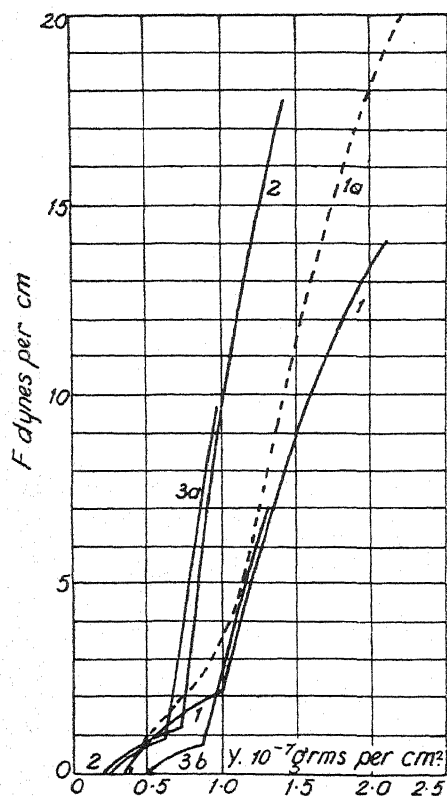


FIG. 2.—Compressibility curves of Protein monolayers on $N/100$ sulphuric acid (16° – 21° C.).

1. Gliadin.
- 1a. Gliadin, spread from the solid.¹
2. Zein
- 3a. Insulin—Specimen J.
- 3b. Insulin—Specimen H.

rapidly when the interval before compression is increased. For example, for the high pressure region of films of insulin H, the value of $\frac{\partial \gamma}{\partial F}$ is 7.2×10^{-8} cm.⁻² sec.² for an interval of two hours, but 0.9×10^{-8} cm.⁻² sec.² for an interval of fourteen and a half hours.

The electrical homogeneity of the films in the regions 2 and 3 has been

¹³ Cf. Crowfoot, *Nature*, 1935, 135, 591.

repeatedly confirmed by measurement of the phase boundary potentials. In the case of gliadin, macroscopical inhomogeneity appears for values of γ slightly less than the limiting density.

The optical homogeneity of the monolayers has been demonstrated by the dark ground ultramicroscopic technique introduced by Zocher and Stiebel.¹⁴ The earliest evidence of collapse appears to be a slight brightening of the field which occurs at a surface density somewhat less than that corresponding to collapse of the surface pressure. For example, for gliadin monolayers brightening of the field occurs at $\gamma = 1.8 - 2.0 \times 10^{-7}$ gms. per cm.², while collapse of the surface pressure is first observed at $\gamma = 2.1 \times 10^{-7}$ gms. per cm.². Longitudinal folds parallel to the edges of the compressing side do not occur very frequently with the proteins studied, and are seen only at areas very considerably smaller than those corresponding to the onset of collapse.

The mechanical properties, of the monolayers are summarised in Table II. It is evident that in the case of gliadin, the monolayers obtained

TABLE II.

Protein.		Gliadin.	Zein.	Insulin (J).	Insulin (H).
Limiting area	γ (gm./cm. ²) δ (Å.)	0.35×10^{-7} 2.6	0.21×10^{-7} 1.6	0.25×10^{-7} 1.9	0.50×10^{-7} 3.8
Limiting area of high pressure region, extrapolated to zero pressure	γ (gm./cm. ²) δ (Å.)	0.85×10^{-7} 6.4	0.67×10^{-7} 5.0	0.57×10^{-7} 4.3	0.81×10^{-7} 6.2
Collapse point	γ (gm./cm. ²) δ (Å.) F (d/cm.)	2.1×10^{-7} 15.8 14.1	1.4×10^{-7} 10.5 17.7	0.95×10^{-7} 7.3 9.7	1.3×10^{-7} 9.9 6.9

are almost identical with those prepared by Hughes and Rideal.¹ The limiting density is the same in the two cases— 0.35×10^{-7} gm./cm.² for films spread from solution, and 0.36×10^{-7} gm./cm.² for films spread from the solid proteins; the approximate thickness at the limiting area is 2.6 Å. The limiting density for the high pressure region is 0.81×10^{-7} gm./cm.² for films spread from the solid and 0.85×10^{-7} gm./cm.² for those spread from solution. Hence it must be assumed that true homogeneous monolayers of proteins with reproducible physical properties can be obtained both by the modified Gorter and Grendel method and by the method of Hughes and Rideal.

It is of interest to note the great difference between the properties of monolayers of the two specimens of insulin. This difference cannot be attributed to incomplete spreading of specimen H since this gives monolayers of identical properties when spread from a solution containing either 11.0 mgm./100 c.c. or 2.9 mgm./100 c.c.

Discussion.

The observed properties of macromolecular monolayers must be interpreted in terms of the properties of the repeating units in the molecule which, in the case of proteins and according to the Fischer-Hofmeister peptide theory, are the CO—NH—CHR residues. The differences between individual proteins must be ascribed not only to chemical differences in the side chains R, but also to differences in the linear sequence of the residues. In discussing the experimental results

¹⁴ Zocher and Stiebel, *Z. physik. Chem., A*, 1930, **147**, 401.

the arithmetic mean properties per residue are calculated from the analytical data, so that, to a first approximation, differences in the amino acid pattern are ignored. In Table III. are summarised the mean proper- ties per residue of the proteins studied.

TABLE III.

Protein.	Gliadin.	Zein.	Insulin.
Mean molecular weight per CO—NH—CHR	120 (Tab. Biol.) 122 (Chibnall.)	106	137
Calculated mean length of side chain in Å.	3.51	3.48	4.24
Percentage of Polar side chains	59.8	38.5	59.8
Mean area per CO—NH—CHR at limiting area in sq. Å. (Calc.)	56.5 (Obs.)	83.2	90.5 (J) 45.2 (H)
Mean area per CO—NH—CHR at limiting area of high pressure region, in sq. Å. (Obs.)	42.5	42.5	47.5
Mean cross-section of head per CO—NH—CHR in sq. Å. (Calc.)	23.3	26.1	39.4 (J) 27.8 (H)
Mean area per CO—NH—CHR at collapse point in sq. Å. (Obs.)	23.8	23.0	24.2
Approximate calculation	9.5	12.5	23.8 (J) 17.4 (H)
	15.2	9.6	15.8

Many analytical studies have been made of the products of hydrolysis of the gliadins from wheat, and critical compilations of

the results have been given in *Tabulae Biologicae*¹⁵ and by Chibnall.¹⁶

The values given in *Tabulae Biologicae* account for 90.7 per cent. by weight of the initial material while those of Chibnall account for 98.4 per cent. : the slight differences between the two sets of analyses lead to no significant differences of interpretation. The analytical data for zein were taken from compilations by Kestner¹⁷ and Waldschmidt-Leitz,¹⁸ and account for 101.3 per cent. by weight of the initial protein. The data for insulin were given by Jensen and Wintersteiner,¹⁹ and account for 88 per cent. ; further, qualitative studies by Jensen and Evans²⁰ were also considered.

The mean length of the side

TABLE IV.

Amino Acid.	Length of Side Chain, (Å).	Cross-Section of Terminal Group of Side Chain. (sq. Å).
Glycine . .	0	20.6
Alanine . .	1.27	20.6
Valine . .	2.5	20.6
Leucines . .	3.7	20.6 *
Phenylalanine	5.3	24
Tyrosine . .	6.5	24
Cystine . .	2.5	34
Proline . .	2.5	24
Aspartic acid.	2.5	25
Glutamic acid.	3.7	25
Tryptophane .	7.5	34
Arginine . .	7.6	26
Lysine . .	6.3	32
Histidine . .	5.3	24

* Effective cross-sectional area.

¹⁵ *Tabulae Biologicae*, Junk, Berlin, 1926, 3, 263.

¹⁶ *Private communication*, 1933.

¹⁷ Kestner, *Chemie der Eiweisskörper*, Braunschweig, 1925.

¹⁸ Waldschmidt-Leitz, *Neuere Untersuchungen über den Aufbau der Eiweisskörper*, Leipzig, 1931.

¹⁹ Jensen and Wintersteiner, *J. Biol. Chem.*, 1932, 98, 281.

²⁰ Bernal, *Z. Kryst.*, 1931, 78, 363; Adam, *The Physics and Chemistry of Surfaces*, Oxford, 1930; Jensen and Evans, *J. Biol. Chem.*, 1935, 108, 1; Meyer and Mark, *Der Aufbau der hochpolymeren Organischen Naturstoffe*, Leipzig, 1930; Robertson, *Chem. Rev.*, 1935, 16, 417.

chain—measured from the carbon atom of the main chain in a direction normal to the axis of the chain—and the mean cross-section of the terminal group of the side chain are calculated on the assumption of the values ²⁰ in Table IV. Proline is assumed to be a unit in the main chain,²¹ and the S-S linkage of cystine is assumed to be a cross linkage between two main chains.

The fundamental assumption implicit in these calculations and in previous discussions of protein monolayers is that only a negligible proportion of the protein spread escapes into the substrate. The correctness of this hypothesis is supported by several lines of evidence:—

1. Compressibility curves identical within the limits of experimental error are readily obtained under a wide range of experimental conditions by spreading from solutions of concentrations varying from 0.01 per cent. to 0.001 per cent. w/v. Further, in the case of gliadin, the monolayers obtained by spreading from dilute solutions are identical with those spread from the solid protein.

2. Protein films do not accumulate on cleaned portions of the surface—enclosed between slides and adjacent to the monolayer—even after intervals of six hours, provided that the surface pressure of the monolayer is considerably below the collapse point. When, however, the surface pressure is raised to produce collapse, protein films appear on the cleaned areas within half an hour.

3. Gorter's experiment on monolayers of pepsin and trypsin ²² not only shows that surface denaturation, if it occurs, is reversible but also demonstrates that less than 20 per cent. of the enzyme spread escapes into the substrate.

These results suggest that an energy of activation exists for the penetration of proteins from the surface layer into the bulk of the substrate. The presence of such an energy of activation is to be anticipated for the transference of the dipoles of the protein molecules through the partially oriented layer of polar water molecules near the interface.

The data summarised in Table III. indicate the general correctness of the picture of the structure of protein monolayers at an air-water interface advanced by Hughes and Rideal¹ but certain modifications are necessary. At the limiting area the main chains are extended on the surface in the β -keratin configuration²³ and all the side chains lie in the plane of the surface. Two types of packing arrangement are possible: (1) regularly arranged parallel main chains (see Fig. 3), and (2) irregularly arranged tortuous main chains which probably cross one another, the configuration of the monolayer then resembling a tennis net. For the regular arrangement (1) the mean area per residue can be calculated on the assumption that the distance of closest approach of the extremities of the side chains of adjacent main chains equals the distance of closest approach deduced from the mean cross-section of the terminal groups of the side chains (approximately 24 sq. Å.); thus the mean area per CO—NH—CHR residue at the limiting area is given, in sq. Å. by: $3.5 \times (4.2 + 0.9 + 2 \times \text{mean length of side chain in Å.})$. The experimental results in Table III. show that in the case of gliadin and of insulin (specimen H) there is agreement between the calculated and observed limiting areas. Presumably in these instances

²¹ Linderstrom-Lang, *Trans. Faraday Soc.*, 1935, **31**, 324.

²² Gorter, *Proc. Roy. Soc., A*, 1936, **155**, 706.

²³ Cf. Astbury and Woods, *Phil. Trans. Roy. Soc., A*, 1933, **232**, 333.

the configuration of the monolayer approximates to the regular arrangement depicted in Fig. 3. For the other proteins, the arrangement must be much more irregular. It is conceivable that regular packing is favoured by a regularly repeated linear sequence of amino acids in the main chains, and that the difference between the two specimens of insulin may be due to differences in the amino acid pattern. The tendency to an open packing arrangement in monolayers of insulin is probably due to the high cystine content.

On compression of the film, the terminal groups of the polar side chains maintain their relation to the water surface, being pushed to-

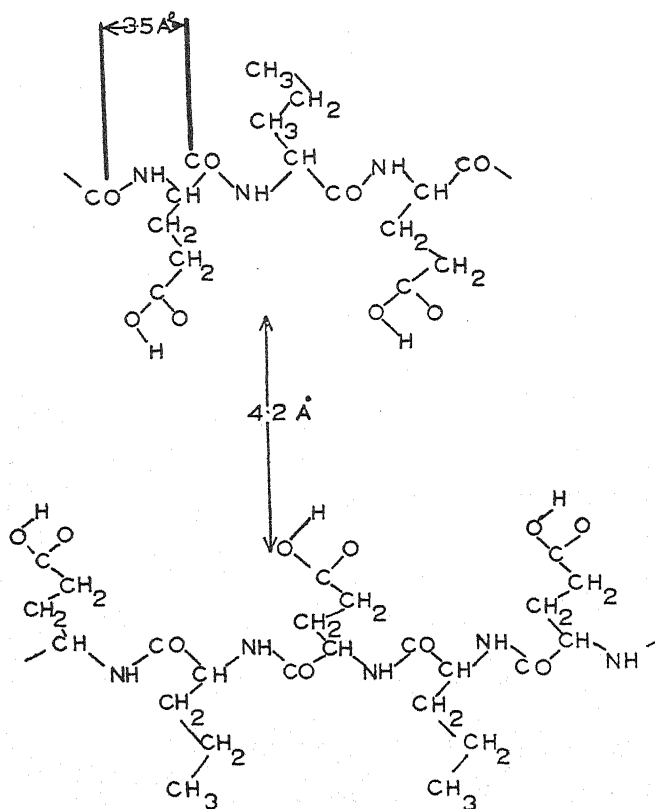


FIG. 3.

gether beneath the main chains which are then lifted up. The non-polar side chains are forced out of the surface, so that compression of the film results in a separation of the polar and non-polar side chains respectively below and above the main chains. The occurrence of this process corresponds to the low pressure region of the F - γ curve and its completion to the inflexion point between the low- and high-pressure regions. Hence at the limiting area of the high-pressure region, the mean area per CO-NH-CHR residue must equal the mean cross-section of the terminal group of the side chain. Table III. shows that a close agreement is found except in the case of the specimen J of

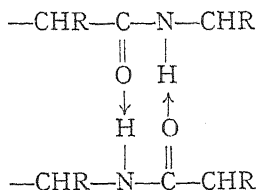
insulin, where it must be assumed that the irregular packing of the chains is still effective. It is evident that at the limiting area of the high pressure region the linear sequence of the amino acid residues is of little importance since the side chains are now normal both to the axis of the main chain and to the surface.

During compression of the film in the high-pressure region one must envisage the possible occurrence of three processes, dehydration, actual compression of the side chains and folding of the main chains in a plane normal to the surface. The importance of dehydration has been emphasised by Hughes and Rideal,¹ who remark on the contribution of the swelling pressure to the total surface pressure in this region. However, dehydration and compression of the side chains are not the only processes occurring, since then the mean area per residue at the collapse point would be of the order of $3.5 \times 4.6 = 16.1$ sq. Å., which is a value somewhat too large. Hence it must be assumed that an irregular plication of the flexible main chains occurs in a plane normal to the surface, with the production in places of a configuration approximating to that of α -keratin. The linear sequence of the amino acids is probably of importance in determining the structure of the monolayers near collapse. If there is a regular alternation of the polar and non-polar side chains, the mean area per residue at collapse must be of the order of the product of the mean cross-section of the head of the polar side chains and the fraction of the total number of side chains with polar terminal groups. If, however, all the polar side chains are arranged in adjacent positions in groups, or if there is a large excess of non-polar side chains, the area per residue at collapse must be considerably greater than that calculated on the assumption of regular alternation. Because of the experimental difficulties at the collapse point, the degree of plication of the main chains cannot be accurately determined, but the data shown in Table III. suggest the possibility of an approximation to regular alternation of the polar and non-polar side chains in insulin H; the excess of non-polar side chains in zein is also in qualitative agreement with the observed mean area per residue at collapse.

These conceptions suggest that the protein monolayers in the high-pressure region possess a triplex structure (*cf.* Rideal, 1936). There is a superficial hydrophobic layer, of thickness of the order of 3.5 Å., formed by the non-polar side chains, then a layer containing the main chains and associated water molecules, and finally, below this, the layer of polar side chains. The physical reality of the hydrophobic surface layer has been demonstrated by Hughes.⁴

As in the case of simpler compounds, the correlation of the physical state of the protein monolayers with the chemical structure presents considerable difficulties, and furthermore, a profound modification of the properties is introduced by the hydration of the molecules. In the low-pressure region the monolayers of most proteins are in the liquid state and are probably two-dimensional sols. Monolayers of myosin spread on Edsall buffer solution have no low-pressure region. The characteristic feature of the high-pressure region appears to be the presence of elasticity and rigidity. These two properties vary greatly in different proteins and do not run parallel; their presence probably indicates that in the high-pressure the films are two-dimensional gels. The physical basis of the gel state is almost certainly the formation of linkages between adjacent main chains at points of varying separation in the different proteins, and it appears probable that such cross-union

between the main chains may be due to the formation of co-ordinated hydrogen linkages between the peptide groups,²⁴ thus :—



Co-ordinated hydrogen linkages may also stabilise the plication of the main chains. The decrease of compressibility on standing is probably due to dehydration, brought about by the van der Waals' attractive fields and the formation of "salt-linkages" between the side chains.

It is evident that for a more detailed analysis of the structure of protein monolayers, the essential requirement is an examination of the properties of relatively simple peptides and their derivatives.

The existence of the triplex structure of compressed protein monolayers at an air-water interface, appears to justify the application of the experimental results to biological systems. Evidence is accumulating that natural membranes frequently consist of a thin lipid layer on the surfaces of which are adsorbed monolayers of proteins.²⁵ The non-polar side chains of the proteins are dissolved in the hydrocarbon layer, whose dielectric constant has the value 2-3, while the polar side chains are immersed in the surrounding aqueous medium. In the triplex protein film at an air-water interface, the molecular environment in the region of the polar groups of the side chains and main chains, which is formally described by the "apparent dielectric constant" in the film (5-10), cannot differ significantly from that in the model membranes at a liquid/liquid interface. Hence in both cases the chemical behaviour of the protein monolayers must be essentially the same.

Summary.

An attempt is made to correlate the macroscopic properties of protein monolayers, spread at an air-water interface, with the chemical structure and molecular configuration by means of the X-ray crystallographic data and the results of experiments on monolayers of simple compounds. Monolayers of three proteins—a wheat gliadin, zein and insulin—whose products of hydrolysis are almost completely known are examined by the surface pressure method, supplemented by observation of the phase boundary potentials and dark ground ultramicroscopy.

The properties of the monolayers, prepared by spreading from solution, vary with the concentration of the protein solution used and attain limiting values at low concentrations (0.01-0.001 per cent.). True homogeneous monolayers of approximate minimum mean thickness varying from 1.6 to 3.8 Å. are prepared by spreading from dilute (0.01 per cent.) solutions and then allowing prolonged time intervals (one to thirty-six hours) before observation. In the case of gliadin the monolayers obtained are almost identical with those prepared by spreading from the solid. It is clear that essentially the same results are obtainable both by the method of Hughes and Rideal and by the technique of Gorter and Grendel modified as described.

²⁴ Sidgwick, *Annual Reports Chem. Soc.*, 1933, 30, 110; *ibid.*, 1934, 31, 37.

²⁵ See e.g., Danielli and Harvey, *J. Cell. Comp. Physiol.*, 1935, 5, 483; Danielli, *Proc. Roy. Soc., A*, 1936, 155, 708.

The mechanical properties of the monolayers are analysed in terms of the mean properties per CO—NH—CHR residue and the structure of the monolayers is discussed. The two most characteristic mechanical criteria are the limiting area, and the limiting area of the high-pressure region. The latter corresponds to completion of the process of separation of the polar and non-polar side chains below and above the main chains, so that in the high-pressure region, the monolayer has a triplex structure. Plication of the main chains appears to occur, and it is suggested that co-ordinated hydrogen linkages may be formed between the peptide groups of adjacent main chains. An attempt is made to assess the rôle of the linear sequence of the amino acid residues in determining the macroscopic properties of the monolayers.

The validity of the application to biological systems of the results obtained with protein monolayers at an air-water interface is briefly considered.

I wish to record my gratitude to Professor E. K. Rideal, F.R.S., for his interest and advice during this investigation.

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THE ACTIVATION ENERGY OF DIFFUSION THROUGH NATURAL AND ARTIFICIAL MEMBRANES.

By JAMES FREDERIC DANIELLI.

Received 22nd March, 1937.

In diffusion through a membrane, whether homogeneous or of a pore-structure, the penetrating ion or molecule encounters potential barriers. These potential barriers can be crossed only if the penetrating body has more than a minimum kinetic energy $\frac{1}{2}mv^2$. From this it can be deduced

that the rate of penetration $R = \frac{N_0}{2v} \sqrt{\frac{2kT}{\pi m}} e^{-\frac{mv^2}{2kT}} \times \text{const.}$ where N_0 is the number of molecules in volume v . And the temperature coefficient

of the rate of penetration is given by $Q_{10} = \sqrt{\frac{T_2}{T_1}} e^{\frac{mv^2}{2k} \left(\frac{10}{T_1 T_2} \right)}$. From either of these equations one can obtain $\frac{1}{2}mv^2$ which is the height of the potential barrier.

From the equations, it follows that for a given structure the slower the rate of penetration, the greater will be Q_{10} and also $\frac{1}{2}mv^2$. This prediction is borne out with some accuracy both by living and inanimate membranes, e.g. collodion, zeolite, chitin, membranes, and by the membranes of erythrocytes, sea-urchins, and large plant cells. Certain apparent exceptions to the rule with living cells propound some fascinating problems in cellular specificity.

In the case of penetration of ions the potential barrier may be mainly electrostatic and its magnitude E in volts can be calculated from $\frac{1}{2}mv^2$. A similar calculation can also be made for polar molecules by assuming a value for the divergence of the potential barrier, and there is a surprising

degree of agreement between the values of E for a variety of different molecules. The value of E appears to be typical for a given type of cell of a given species.

By measuring $\frac{1}{2}mv^2$ (the activation energy) for molecules both entering and leaving the cell a significant measure of the membrane asymmetry is obtained. There may be a considerable difference between these activation energies, e.g. 4000 calories for $\left[\left(\frac{mv^2}{k} \right)_{\text{entry}} - \left(\frac{mv^2}{k} \right)_{\text{exit}} \right]$ for eggs of the sea urchin *Arbacia*. This means that the membrane can maintain concentration differences by utilising the heat energy of its surroundings. As this type of behaviour has been reported also in the inanimate chitin Crustacean membranes, it appears that we may have here a weapon for investigating the physico-chemical basis of cellular secretory activity.

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GENERAL DISCUSSION.*

Dr. G. S. Adair (Cambridge) said: Differences of opinion have been expressed on the question whether membranes of parchment, collodion and similar substances can give the same equilibrium as an ideal membrane, permeable by crystalloids but impermeable by colloids. Svedberg and Sjögren¹ stated that the sources of error in osmotic measurements are numerous and uncontrollable. Adair,² on the other hand, found that certain types of collodion membranes appeared to give a close approximation to ideal membranes, in that the pressures reached a steady value in a short time, and remained constant for weeks, and returned to the same value after resetting. Further investigations have shown that such membranes can retain hæmoglobin for long periods. No hæmoglobin could be observed in the dialysate after four years, and only a trace after nine years.

Some membranes adsorbed appreciable amounts of the protein whereas others showed no signs of adsorption, but after allowing for the changes in concentration determined after equilibration, the osmotic pressures were the same.

The question whether the specific properties of the membranes affect the membrane potentials³ has been re-investigated by placing samples of solutions of protein chlorides and hydrochloric acid on opposite sides equilibrated by means of a large membrane on opposite sides of small membranes of permeabilities ranging from 0.50 to 0.005.⁴ It was found that the potentials were not affected by relatively large changes in the permeability of the membranes. The permeabilities are expressed in c.c. of water forced out in one minute by a pressure of 450 mm. of mercury, for membranes 10 cm. long, 1.1 cm. in diameter and approximately 0.008 cm. thick. In systems where diffusion is taking place, the permeability is of great importance. Membranes of the permeabilities of 0.5, 0.043 and 0.005 respectively separating solutions of 0.1 and 0.01 Molar KCl

* On 8 preceding papers.

¹ Svedberg and Sjögren, *J. Amer. Chem. Soc.*, 1928, **50**, 3318.

² Adair, *Proc. Roy. Soc. A*, 1925, **108**, 627.

³ Adair and Adair, *Biochem. J.*, 1934, **28**, 199.

⁴ The permeability of the membranes was altered by adding different amounts of ethylene glycol to the collodion solution, which was poured over the outside of a rotating glass mould. See ref. (2) also *Practical Physiological Chemistry*, S. W. Cole, Cambridge, 1933.

gave potentials of 1.9, 8.1 and 19.3 millivolts respectively. The observations of the membrane potentials cover a wider range of permeabilities than the osmotic measurements, which were restricted to membranes from 0.15 to 0.01.

Dr. T. Teorell (*Uppsala*) said: The membrane equilibrium, as discussed by Dr. Adair, is of the well-known type ascribed to Donnan (Gibbs). It rests on the assumption that at least one of the charged constituents is non-diffusible through a given boundary (in general being a membrane). The system considered as a whole is in a true thermodynamical equilibrium. This type of membrane effect may be of importance in relation to a great many biological conditions. Living cells or tissues, however, are in states of non-equilibria or steady states. In other words, dynamical components have to be considered. In another connection,⁵ it has been shown that differences in mobility of the ions of a steadily diffusing agent may produce a distribution of other ions of the same type as is characteristic for the Donnan effect, although *all* constituents may be *freely diffusible*. When considering the genuine Donnan effect or the "diffusion effect" alluded to, interest has hitherto been given only to the concentrations in the two *bulks* surrounding the membrane. However, it may be of importance to consider also the conditions *within* the transition layer, *i.e.*, the ionic distribution within the membrane itself and the course of the electrical potential gradient there.

Some figures are reproduced below in order to demonstrate that remarkable effects may occur within membranes across which some steady diffusion takes place. The diagrams (somewhat schematic) have been drawn on the basis of results (as yet unpublished) obtained with a special device for the investigation of diffusion layers.⁶

The explanation of these observations has to be ascribed to the combined influence of "osmotic" and electrical forces.⁷ The membrane is in these cases the site of a potential, here identical with a common diffusion P.D. The courses of the potential gradients were also investigated, but are omitted in the diagrams. Incidentally, it may be mentioned that Planck has theoretically predicted the existence of a case somewhat similar to diagram (b).

In the genuine Donnan effect the protein has been regarded as a "fixed" constituent rearranging the electrolyte picture in a membrane system; in the systems sketched here a reverse situation occurred. It was found that the distribution of a protein can be easily influenced by diffusible electrolytes. Thus we encounter new forms of membrane equilibria, or, more correct, steady state phenomena in membrane systems, which might be of biological significance.

Dr. J. H. Schulman (*Cambridge*) said: The mechanism of the associations between polar groups in orientated molecules giving the stability to monolayers in general may be based on a dipole-dipole or ion-dipole or ion-ion interactions, according to coulomb forces.

I. Thus dipole-dipole interaction $E = \frac{\mu\mu}{r^3} \cos \phi$ is very much weaker

II. than ion-dipole interaction $E = \frac{e\mu}{r^2} \cos \phi$,

III. which is weaker than ion-ion $E = \frac{e^+e^-}{r}$,

IV. repulsion coming from ion-ion interaction of ions of the same sign.

Dielectric constant is omitted from the formula, since it is included in μ calculated from $\Delta V = 4\pi n\mu$.

⁵ P. 983.

⁶ "Multi-membrane" method, *J. Biol. Chem.*, 1936, 113, 735.

⁷ Cf. pp. 920 and 1054.

Films composed of type I. can exist over all states.

Films of type II. are all in solid condensed state.

Films of type III. are gel-like structure proteins or solids.

Films of type IV. are all in vapour state.

The assumption is made that in all four classes mentioned the Van der Waals' forces are of the same order. Differences between the observed and calculated surface pressures and surface potentials of mixed

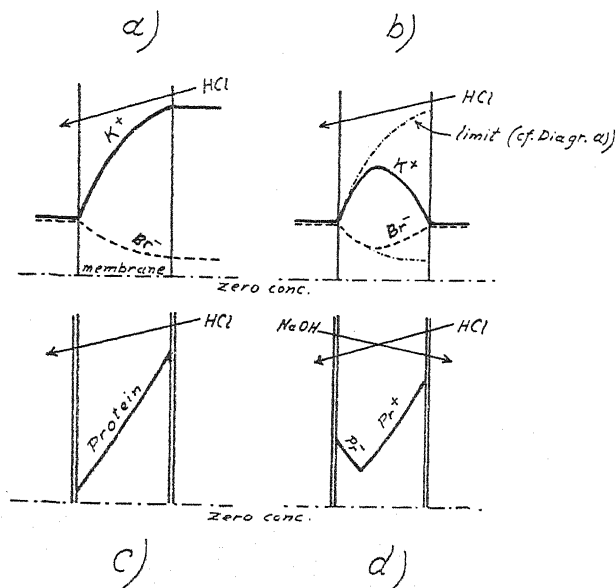


FIG. 1.—The arrows show the direction of the steady stream of the diffusing agent. The heavy or dotted lines show the distribution in the steady state of the "passive" ions, the height over the zero line indicates concentration.

- Volume left is large (*i.e.*, composition constant), right small. This diagram corresponds to a fully established "diffusion effect." Note that $(K \times Br)_{\text{left}} = (K \times Br)_{\text{right}}$.
- Surrounding solutions kept constant in composition (volumes large). Note the accumulation of K and the impoverishment of Br. within the membrane.
- The membrane contains a protein (initially equally distributed). The membrane surfaces, however, are impermeable to the protein. Note the marked redistribution of the protein due to the HCl diffusion.
- The same as (c), but this is a case of *interdiffusion* (NaOH diffusing from left). The peculiar protein distribution within the membrane is a consequence of the fact that the protein particles have opposite charges to the left and the right, because of differences in p_H .

films composed of different polar groups but equal chain lengths mentioned in my paper all fall into the following classifications,

$$III > II > I > IV.$$

ϕ = angle between the resolved moments of the two polar groups, E = energy of association, r = distance between charges and, μ = dipole moment as measured by surface potential.

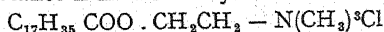
Dr. N. K. Adam (London) said: I would like to see attention paid to the more precise definition of the term "denaturation" of a protein. It seems to be rather loosely employed to denote some change which tends to render the protein less soluble. Ramsden found that adsorption of some proteins at a surface renders them insoluble, and called this denaturation. If proteins are denatured by heat in bulk, they are no longer

able to spread at a water-air surface (Neurath). Complete spreading consists probably in an unfolding of the molecules to a thickness of the order 5 Å, in which it must be stretched out to a considerable extent, very likely to a layer one amino-acid thick on the water-air surface. When it becomes insoluble as a result of this spreading, or by adsorption at the surface, it seems that the molecule is fixed in this configuration in some way, and cannot again roll up to a form suitable for bulk solution. When a protein is in solution in a bulk phase, it is in much thicker aggregates than when spread. Many ordinary proteins can be spread from such solutions; the forces holding the protein particles rolled up tight in the bulk solution are therefore not very strong. After denaturation, as the same proteins will then not spread, it would appear that the forces holding them as more or less spherical aggregates have been tightened as a result of the denaturation. In much the same way, Professor Gorter's myosin or fibrinogen do not spread; however after slight digestion with proteolytic enzymes they do spread. They may perhaps not have been broken up into smaller molecules, by actual splitting of the peptide linkages; perhaps all that the enzymes do in facilitating spreading is to loosen the bonds (of probably a "residual valency" kind) which have been tightened in the denaturation process, or are naturally tight in the case of the myosin and fibrinogen. These remarks are made much more in the hope of suggesting a certain point of view for consideration and experimental test, than with any conviction that they do actually represent the state of affairs.

Dr. J. D. Bernal (*Cambridge*) said: Although I have never worked with protein films, I feel that some help to understanding their structure may be obtained from X-ray studies. It is not at all clear that the average thickness of the films, as measured from their area, represents their thickness at any point. Indeed, there is as yet insufficient evidence for supposing them to be uniform and not mosaic films. If, however, we make this assumption, there are only two possibilities for their formation. The first is the polypeptide chain. This I consider excessively improbable. The formation of such chains from globular protein molecules could only take place by a kind of unwinding process, as of a ball of wool, which is physically inconceivable. Nor would polypeptide chains give surface films at all, because owing to their flexibility the hydrophilic groups would be equally available on all sides and true solution rather than surface adsorption would take place. This is probably the explanation of the failure to obtain films from proteins known to have such chain molecules. The other alternative is that the globular molecule, which for a normal protein has dimensions $30 \times 40 \times 40$ Å, split into layers each having sides of different hydrophilic properties, are adsorbed on the surface. This is certainly strongly suggested by the experiments of Langmuir and Wrinch, though I see little probability in the process suggested by the latter for the formation of such layers. It is also in accord with the X-ray evidence which shows that all proteins so far examined on particularly strong reflection at about 10 Å correspond to a layer of thickness presumably determined by amino acid residues. I think, however, it would be premature at this stage to attempt to draw from the film evidence anything but the most general confirmatory evidence on protein structure.

Dr. M. Mathieu (*Paris*) (*communicated*): The relation between the extension of parilline and red cell lipoids is a very striking fact.

Dr. Baranger, in Paris, is now working on hæmolytic substances, to see how the hæmolytic power is connected with the structure of the molecules. For instance if in the stearylcholine

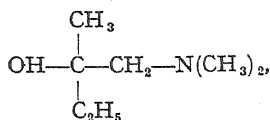


we replace a tertiary amine in the choline



we get the stearyldiamonoethanol. Its hæmolytic power is four times smaller than that of stearyl choline.

With a branched base such as



the hæmolytic power falls to nearly forty times less than that of amino-ethanol stearate. This shows that the long chain molecule is not the only factor of the hæmolytic power.

May I ask Professor Gorter what he thinks of extending experiments on these substances? Shall we find a relation between their surface and the surface of the destroyed red cells?

Continuing some work started by Delezenne and E. Fourneau, Baranger⁸ thinks that the hæmolytic power of *any* substance is closely related to the power of that substance to associate with cholesterol. The more stable the association, the greater is the hæmolytic power.

Sometimes these complex compounds between long chain compounds and cholesterol are very well crystallised. The study of the action of water on the crystals is very fascinating. I am now doing it on the same lines as those I used for studying the action of ketones or nitrocellulose fibres and films. Even now I can be sure of the truth of what Professor Krogh says in the first lines of his paper: "an active transport of a substance is brought about by some kind of 'dynamic machinery.'"*

I found exactly the same thing with nitrocellulose films. Immediately after contact with ketone vapour, the film is no longer nitrocellulose but a compound (if we want to keep the film we must lower the tension of the active ketone).

To sum up I think that not enough work has been done from a purely chemical point of view. Much could be known by working on the chemical reactivity of pure substances chosen as similar as possible as those which are supposed to play the most important part in the permeability phenomena.

Dr. J. H. Schulman (*communicated*): I should like to quote from my experiments⁹ showing the remarkable effects of hæmolytic and agglutinating agents on films of cholesterol and protein and their mixtures. Summarising: it was found that all hæmolytic agents (such as saponin, long chain carboxyl and sulphate fatty acids, taurocholic acid or psychosin), either "penetrate" cholesterol and sphingomeylin films or disperse protein films or do both phenomena.

Experimental evidence was given showing that such film "penetration" was due to a strong association between the polar groups (of the ion-dipole type) followed by Van der Waals' adhesion between the non-polar portion of the molecules forming the film and the "injected" molecules, thus forming an equimolecular mixed film. Agglutinating agents on the other hand only adsorb on to protein films by polar interaction, destroying the adhesion of the protein units to the water, by the hydrophobic portion of the adsorbed agglutinating molecule. Further work is in progress in measuring the interactions between biologically active substances and artificial membranes composed of the components of biological systems, utilising the methods of surface pressures and surface potentials.

Dr. O. Gatty (*Cambridge*) said: Caution should be used in interpreting Dr. Danielli's formula. If solubility in an intermediate phase (*e.g.*, a

⁸ *Ann. Physiol. et Physicoch. biol.*, 1937, **13**, 341.

* I would call to mind recent papers, one by Bernal and one recently published in the *Z. Kristallographie* showing that cholesterol itself gives compounds with water. The compounds made by Dr. Baranger with long chain compounds and cholesterol are emulsinated in water only after a reaction of water on the crystals. These compounds are detected by X-ray methods.

⁹ *Proc. Roy. Soc., B*, 1937, **122** and *this vol.*

thin lipid film) plays the part of a necessary prelude to penetration his activation energy will be related to the temperature coefficient of a partition coefficient and will correspond to a heat of transfer from an aqueous to a water saturated lipid phase.

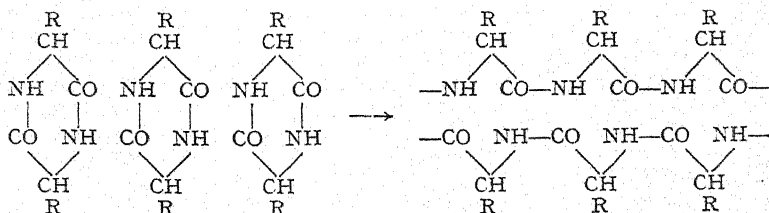
In addition velocity constants for quite simple reactions are not always easy to interpret. For a bimolecular chemical reaction this constant, k , is given by

$$k = P \cdot Z \cdot e^{-E/RT}$$

where the factor $e^{-E/RT}$ is due to the need of an energy of activation, Z is a collision number and P is said to denote the probability of an energetically satisfying encounter leading to chemical change. For bimolecular reactions P is known to be unity for some hundreds of reactions in solution and for some tens of reactions in gases. It may be as high as 10^{-9} or as low as 10^{-9} . Entropy changes, transition probabilities, and geometrical factors have all been considered in accounting for observed values of P .

Professor E. Gorter (Leiden), in reply, said: It would certainly be interesting to extend experiments on the substances studied by Dr. Mathieu. Comparison with our experiments would only be possible if his substances also spread on water. Denatured proteins after slight digestion with proteolytic enzymes do spread at a water-air surface. This fact is in agreement with the view expressed by Adam.

Dr. J. S. Mitchell (Cambridge), in reply (*communicated*): The problem which at present is of fundamental importance in the study of protein monolayers is the correlation of the macroscopic physical properties and the molecular structure. From the examination of monolayers of proteins whose amino acid composition is almost completely known, it is evident that in these cases the observed properties are consistent with a structure composed, at least largely, of flexible polypeptide chains; in the gel state, lateral association of the peptide groups of the main chains appears to occur, probably by means of co-ordinate linkages. Experimental evidence that polypeptide chains (of sufficient length) can form monolayers is provided by the results of the examination of films of polyesters—neutral and acidic ethylene succinates—by Moss¹⁰ and of the tripeptide of α -aminocaproic acid by Gorter, Meyer and Philippi.¹¹ The occurrence, both in monolayers and in native proteins, of substituted diketopiperazine rings, held together by co-ordinate linkages, cannot be excluded and the possibility must be considered that polypeptide chains may be formed from a protein crystal containing diketopiperazine rings by a process analogous to the formation of fibres from crystalline tri-oxy-methylene,¹² thus:



Further, it is not impossible that such a process may occur during the denaturation of proteins.

The most characteristic mechanical criteria of the protein monolayers examined are the extrapolated "limiting densities" of the low and high pressure regions. I wish to emphasise that (as in the high pressure region)

¹⁰ *J. Amer. Chem. Soc.*, 1934, **56**, 41.

¹¹ *K. Akad. Wetensch. Amst.*, 1934, **37**, 55.

¹² Kohlschutter and Sprenger, *Z. physik. Chem., B.*, 1932, **16**, 284.

the limiting density of the low pressure region is obtained by extrapolation to zero pressure. Its value is independent of instrumental factors. An identical value has been obtained, in the case of the gliadin, with three surface dynamometers of different sensitivity and this value has been confirmed by measurements of the phase boundary potential, since the limiting density coincides with the transition between the electrically homogeneous and inhomogeneous regions. The limiting density of the high pressure region shows a variation similar to, but very much smaller than, does the limiting density of the low pressure region. For gliadin in the high pressure region, the limiting density attains an approximately constant value (0.80 mgm. per sq. metre) for spreading solutions of concentration 0.1 per cent. w/v; in passing to a concentration of 1 per cent., the apparent value increases to 1.10 mgm. per sq. metre. Accordingly for protein monolayers *in the high pressure region*, there does not appear to be any essential discrepancy between the results presented here and those obtained by Professor Gorter.

It does not seem possible to account for the observed compressibility curves of protein monolayers in terms of the "cyclol" theory of protein structure.¹³

Dr. J. F. Danielli (London), in reply (*communicated*): The activation energy of diffusion is related to an activation energy of a partition coefficient. To say this, however, is simply repeating my statement in different language. What we want to know is the nature and magnitude of the various forces which determine the size of the activation energy; some of these forces may be those encountered at a phase boundary between lipid and non-lipid. The only way to unravel the problem is to consider the separate contribution of each type of force.

¹³ Wrinch, *Proc. Roy. Soc., A*, 1937, **60**, 59.

(Reports received after going to Press.)

Dr. F. C. Steward (London) (*communicated in reply to Dr. Hartley's remarks on page 1022*): Dr. Hartley's suggestion is interesting. The difficulty is to homologise Dr. Hartley's compartments and membranes with known inclusions and membranes in plant cells, which, though they may possess the minimum of visible complexity yet display the most impressive salt accumulation. It would be easy to homologise compartment X with the vacuole. At least two membrane systems are conspicuous—the inner and outer protoplasmic membranes, and these bound the phase in which the metabolism must occur (compartment Y in the diagram). Most plant physiologists would neither regard the protoplasm as the seat of an osmotic concentration in excess of that in the vacuole nor endow it with the ability to secrete water externally. Difficulty is involved in any view which demands in these simple plant cells that water entry and exit occur in specialised regions. Absorption of water or salts apparently occurs freely over the whole surface but the two processes are independent. If localised areas with the special properties named exist, they have not yet been identified, and, moreover, they must retain their identity in a streaming mass of protoplasm only a few microns thick, which, apart from the minute inclusions which render the movement visible, is free from visible complexity of structure. Although they may not have formulated the idea so rigidly, plant physiologists quite early attempted to explain the salt uptake by the whole plant on the basis of the idea expounded by Dr. Hartley. Salt was supposed to enter "with the water." An obvious mechanism for "secreting water" in the form of vapour is apparent in the leaves. Without embarking upon a difficult discussion it is evident that even here the idea breaks down, because the entry of salt and water are clearly independent and their independence is due mainly to the very property now under discussion, namely the ability of the living cells to accumulate salts selectively.

(*In reply to Professor Krogh's remarks on page 1022*): Professor Krogh refers both in discussion and in his paper to the problem of salt uptake by roots and to the work of Lundegårdh. In particular Professor Krogh cites the conclusion of Lundegårdh that only the absorption of anions bears a relation to metabolism. Papers cited elsewhere¹ show that this is a false conclusion. Work done upon a variety of plants and absorbing systems, and independently, by Steward and Moagland and their respective collaborators, has shown that the uptake of anion and cation are determined by similar variables and both are related to metabolism. The only cases of cation uptake which are independent of metabolism involve mere chemical reactions with those non-living tissue substances which are capable of base exchange. These phenomena are of minor importance on the plant and do not present the problems with which the symposium was particularly concerned.

Professor Krogh touches upon what he terms the "natural function" of roots and lightly dismisses the rôle of growth in the uptake of salt and water and their transfer to the stele. Professor Krogh could hardly have chosen a more unfortunate case to prove his point. The mechanism of transfer into the stele is one which is still more obscure than the initial accumulation of salt by the cortical cells. The latter process can now be accurately described by reference to recent work.² The latter still needs careful investigation with due regard to the structure and development of roots. Contrary to Professor Krogh's implication the only quantitative investigation³ on the distribution of accumulation in roots did reveal a pronounced longitudinal gradation which reflected the distribution of the actively growing cells. The absorption of salt by the excised root is conditioned by at least two internal variables in addition to the external factors described by Moagland and Broyer. These internal factors are (a) the stage of development of the cells concerned, (b) their salt content, which is in turn determined by the previous nutrition of the plant and also by the removal of salt from root to shoot. The property of absorption is maintained in the attached root longer than in the excised root, partly because the former continues to grow but also because the more active tissues of the shoot are able to deplete the root of salts. The salts which migrate from root to shoot are absorbed by the most actively growing portions of the shoot. It is a very superficial view which regards the salt uptake by the root as independent of growth.

¹ See page 1006 *et seq.*

² See papers by Moagland and Broyer and by Prevot and Steward.

³ Prevot and Steward.

CONCLUSION.

BY ERIC K. RIDEAL.

In this discussion, emphasis has been laid on several different problems, the structure of natural membranes, their apparent selectivity in permeability and the origin of the difference in potential, chemical, osmotic or electrical which effects and maintains a difference in activity across the membrane. Closely allied to this is the problem of bioelectric potentials in which not only are potential differences maintained, but the systems appear to have no small electrical capacity. It is clear that in some cases the membranes may be no more than orientated monolayers, in others a discrete phase, separated from the larger bulk phases by orientated monolayers, exists. Clearly the mechanism of passage, of storage, and causes of stability and potential difference are not identical for these two cases, and progress from the physico-chemical side must involve consideration of each type.

Attempts to divide all membranes into sieve and homogenous phase types respectively, including those consisting of two phase mosaics, do not appear to be sufficiently comprehensive, and it is possible that we may have to extend our classification to include those in which there are solubilising or reactive groups separated from one another in a bulk phase. Migration through such a system would consist of a series of jumps from active group to group. Many cases of such migrating processes are known in other fields.

The establishment of a Donnan distribution between two phases, one of which possesses a finite and limited volume (the membrane) appears certain in many cases. Alterations in ionic distribution may be brought about by change in ionic concentration but also by change in the free volume; this can be effected by non-electrolytes reacting with the bonding of the gel fabric.

The meeting has served a useful purpose in giving us an account of a really large subject, but in future discussions on this topic it might be well to limit the enquiry into some much more limited aspect of this extensive field.

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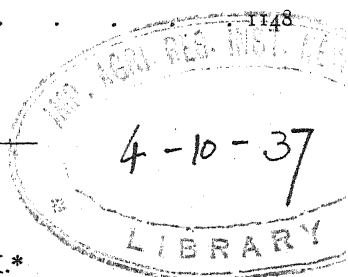
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THE CORROSION OF TIN IN NEARLY NEUTRAL SOLUTIONS.

By T. P. HOAR.

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1. Introduction.

Tin, tin-rich alloys and tin-coated metals are widely used as corrosion-resistant materials in contact with neutral and nearly neutral liquids, such as water, milk and certain canned foods. Such corrosion as is found usually takes the form of localised "black spots."¹ This attack is undesirable in practice, for it is unsightly, may lead to contamination, or to the exposure of a basis metal (where a tin coating is concerned). It is also of scientific interest, especially since localised corrosion has not been investigated in such detail as the severer attack found on such metals as iron and zinc.

Brennert² has studied the formation of black spots on tin in sodium chloride, sulphate and nitrate solutions. A necessary preliminary to the formation of black spots is an actual *building up* of the oxide-film originally present on the tin surface, with consequent ennobling of its electrode potential. Only when the potential exceeds a certain value can film breakdown and black-spot formation occur. Brennert has also found by chemical analysis that the corrosion product consists principally of stannous oxide, with some 20 per cent. stannic oxide. Similarly Bannister³ has reported that the corrosion product on an ancient specimen of pure tin contained 43 per cent. hydrated stannous oxide and 55 per cent. anhydrous stannic oxide.

In the present work, the influences of the surface condition of the tin and the concentration of chloride ion on black-spot formation have been investigated, and a detailed mechanism for the process is proposed. The attack by nearly neutral solutions containing numerous different anions and cations has been studied; the results support and extend the suggested mechanism, and may have value in themselves in exemplifying the corrosion of tin under very various conditions.

2. Materials and Technique.

The tin mainly used was rolled sheet having as impurities Sb, 0.23 per cent.; Pb, 0.04 per cent.; Bi, 0.02 per cent.; Fe, 0.01 per cent.; S, 0.01 per cent. Some check experiments (see Section 9) were carried out with a pure sample of Chempur tin, whose impurities were Sb, 0.001 per cent.; Pb, 0.006 per cent.; Bi, 0.003 per cent.; Cu, 0.001 per cent.; Fe, Ni, As, Ag, < 0.001 per cent. The "as rolled" surface was further prepared, except where otherwise stated, by a light abrasion with Hubert 1F emery-paper. This method gives a reproducible surface when conducted uniformly by a practised operator.

¹ W. Mohr and M. Schulz, *Milchwirtschaft. Z.*, 1930, 26a-28a, 1037.

² S. Brennert, *Tech. Pub. Int. Tin. Res. and Dev. Council*, D, No. 2 (1935).

³ C. O. Bannister, *J. Inst. Met.*, 1926, 35, 71.

The corroding solutions were prepared from distilled water condensed on Pyrex, and B.D.H. "Analar" materials. In the few cases where these are not available, "pure" salts were used.

The corrosion technique was similar to that previously adopted.⁴ Strips of tin, 6.5×2.5 cm., were prepared as hereinafter described, the final operation being a degreasing with carbon tetrachloride. They were then coated with paraffin wax for a length 3.0 cm. from the top, leaving $3.5 \text{ cm.} \times 2.5 \text{ cm.}$ of the metal exposed. The corrosion experiments were conducted in a thermostat room held at $25.0 \pm 0.3^\circ \text{C.}$ Immediately before the commencement of the experiment, each specimen was clipped to a waxed nickel-plated copper holder H (Fig. 1), which was rigidly fixed to a 270 c.c. beaker, 11 cm. high \times 6 cm. diameter, with soft red wax. The appropriate corroding solution was then run into the beaker until the top of the exposed part of the specimen was 1 cm. below the liquid-line; the holder for each beaker was previously calibrated so that this depth of liquid gave a volume of 200 c.c. The beakers, twenty in each experiment, were placed after filling in a metal box, 76 cm. long \times 33 cm. wide \times 18 cm. high, fitted with a thick rigid wooden base and a hinged lid. The liquids in beakers holding duplicate specimens were connected electrolytically by means of filter-paper strips moistened with the same liquid.

Measurements of the electrode potential of each pair of duplicates were made at intervals, by connecting the liquid of one of them, through a second filter-paper strip moistened with it, to a saturated calomel half-cell. The e.m.f. of the cell

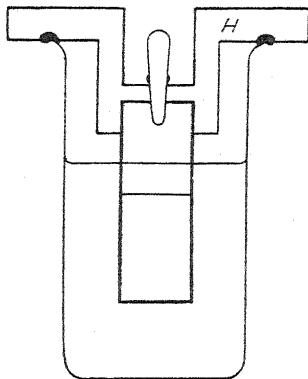
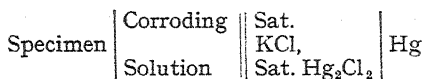


FIG. 1.—Corrosion technique.



was then found by means of a Cambridge Instrument Co. valve electrometer, to an accuracy of ± 1 mv. The second filter-paper strip was removed immediately after the measurement to prevent any diffusion of saturated potassium chloride into the corroding solution. The potentials of the specimens were followed throughout the course of a run. Since under the conditions here studied tin suffers localised attack, the main part of the metal remaining covered with oxide-film, the measured potential is sensibly that of the film, which is cathodic towards the tiny anodic corroding areas. Repair of the film, *i.e.* decrease in the anodic areas and hence of the current flowing between film cathode and metal anode, lessens the cathodic polarisation, and hence raises the measured potential.⁵

The specimens were finally dewaxed and examined.

3. Formation of Black Spots in Chloride Solution.

Typical black-spot formation was produced on specimens of tin prepared by abrasion with Hubert 1F emery-paper and storage for a few days in dry air, when they were immersed in 0.1 N potassium chloride solution. Such specimens possess before immersion a nearly invisible oxide-film due to atmospheric oxidation (see next section). The electrode potential, after an initial very rapid fall to about -0.25 v. (N-hydrogen scale),* rose to a

⁴ T. P. Hoar and D. Havenhand, *J. Iron and Steel Inst.*, 1936, **133**, 239 P.

⁵ L. C. Bannister and U. R. Evans, *J. Chem. Soc.*, 1930, 1361.

* "Noble" metals, *e.g.* silver, are taken as positive to hydrogen.

maximum of about -0.15 v. in a few hours, and then fell slightly, black spots being produced; thus as noted by Brennert,² film repair appears to be an essential preliminary to black-spot formation. After 72 hours, such specimens showed an interference-tint over the whole of the surface other than the black spots, the colour varying with the conditions (see later) from 1st-order yellow nearly to 1st-order mauve. After long attack (20-50 days) the film had thickened further, to show mainly 1st-order mauve and sometimes blue tints. Near the black spot or spots (which increased in size with lapse of time) higher-order interference-tints indicated thicker films than on the remainder of the specimen, colours up to the 3rd order, and even an opaque white deposit, being often found in the immediate neighbourhood of the spot. The thickened film had the general form shown in Fig. 2, being thickest nearest the spot, and is evidently formed by the precipitation of an insoluble body in contact with the film surface,

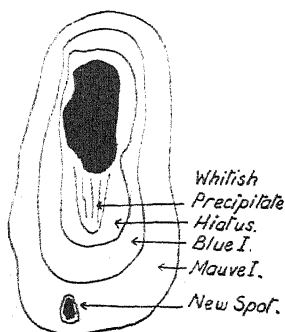
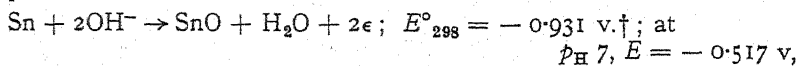


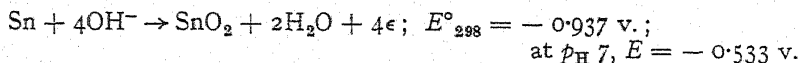
FIG. 2.—Form of black spot and surrounding film.

from a soluble corrosion product spreading outwards and especially downwards from the spot. The phenomenon, noted by Brennert² and in the present work, of preferential formation of new black spots near earlier ones, is probably conditioned by this "secondary" film growth and repair consequent upon the first spot.

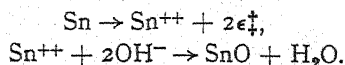
The mechanism of the film repair and ultimate black-spot formation may now be considered. The initial oxide-film surface, acting as an inert basis for the net reaction $O_2 + 2H_2O + 4e \rightarrow 4OH^-$, is cathodic towards the metal at the base of the pores in the film; the initial very rapid fall of potential observed is due to the polarisation of the film cathode by the "local-action" current which begins as soon as the electrolyte has penetrated the pores.⁶ Now, as discussed later (Section 9), the potentials of the Sn, SnO, OH^- and Sn, SnO₂, OH^- metal/metal-oxide electrodes are very much more negative than the standard potential of the Sn, Sn⁺⁺ electrode,⁷ -0.136 v., even in solutions of p_H 7; it is therefore probable that the initial *net* anodic process at the base of the pores is either



or



or a mixture of both these reactions, which have nearly identical electrode potentials. This anodic process of oxide formation perhaps takes place in stages, not involving the direct discharge of hydroxyl ion, thus:



⁶ T. P. Hoar, *J. Inst. Met.*, 1934, **55**, 135.

⁷ G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill), 1923, p. 433; M. Prytz, *Z. anorg. Chem.*, 1928, **172**, 147.

[†] *I.e.* the standard potential on the normal hydrogen scale at 25° C. or 298° Abs.; the notation is that of Lewis and Randall.

[‡] It must be remembered that part of the current in the electrolyte is carried by the anion present, in this case Cl⁻. Nevertheless there is no discharge of

[Footnote continued overleaf.]

On either view the oxide is formed and must be in approximate equilibrium with stannous and hydroxyl ion according to solubility product principles. The very negative metal/metal-oxide standard potential merely indicates that the stannous ion activity, and hence the solubility of the oxide, is very small except in quite acid solutions; the anodically attacked metal is thus almost entirely converted into solid oxide, unless the anolyte becomes acid. Similar considerations apply to the formation of stannic oxide.

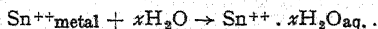
Oxide production within the pores tends to heal them up, with consequent rise of their electrolytic resistance. Less current can flow between the film cathode and the anode at the base of the pores, and the potential of the film cathode—the measured potential—rises. However, as a pore closes up, the current-density at the anode rises, while the replenishment of hydroxyl ion by migration inwards of that produced at the cathode becomes increasingly difficult. The decreasing concentration of hydroxyl ion at the anode involves an increasing concentration of stannous ion and a rise of anodic potential; this allows the cathodic (measured) potential to rise correspondingly. Eventually the anolyte becomes so acid that a considerable proportion of the metal is converted into soluble stannous ion rather than into solid oxide. The pre-immersion oxide-film, so far from being healed with oxide, is now *undermined* by the production of a soluble product from the metal, and breakdown occurs. The metal/metal-oxide reactions can now proceed apace, for as long as a sufficient proportion of soluble stannous ion is also produced, a state of film breakdown and hydroxyl-ion supply is maintained; and while the anodically produced oxides are capable of plugging up a small pore, they cannot form a new protective film at a relatively large breakdown in the pre-immersion film. Thus the rise of measured potential to a maximum (-0.15 v.) not far below the Sn , Sn^{++} standard value (-0.136 v.), its slight fall as film breakdown occurs, and the subsequent production of black spots consisting of stannous and stannic oxides, are readily explained. Moreover, the preliminary uniform thickening of the film is doubtless due to the electrophoresis outwards from each pore of positively charged colloidal stannic oxide and its subsequent coagulation on the film surface by the excess of hydroxyl ion there; while the later non-uniform thickening, greatest near the black spots, is due to the precipitation of the stannous ion produced there as it migrates to the film cathode with its excess of hydroxyl ion, as stannous hydroxide.

Confirmation of this theory of black-spot formation has been obtained in the following further experiments.

4. Influence of the Surface Condition of the Metal.

Abrasion of a metal surface with emery-paper removes any original oxide-film, but owing to the local heating produced, some oxide may be formed *during* the abrasion.⁸ A zone of strained and shattered metal is

Cl^- at the electrode surface; rather it is "neutralised" by the outcoming cation. Modern views of metallic structure lead to



as probably the most rational equation for the anodic dissolution of tin to stannous ions, but the older form is here retained for clarity. See U. R. Evans and T. P. Hoar, *Trans. Faraday Soc.*, 1934, **30**, 424; U. R. Evans, *Metallic Corrosion, Passivity and Protection* (Arnold), 1937, p. 10.

⁸ S. Dobinski, *Phil. Mag.*, VII., 1937, **23**, 397.

also produced, and this at once begins to oxidise in air. The oxide-film formed is continually broken down owing to the stresses in the metal, and thus continues to thicken to give a somewhat non-uniform film until most of the strained material is oxidised; but subsequent film thickening in dry air is probably very slow.

Any oxide-film on tin is readily removed by cathodic treatment⁹ in dilute sodium carbonate solution at a small current-density. Now, if at any time during the oxidation of the shattered zone formed on abraded tin the oxide so far formed is removed by cathodic treatment, the film afterwards formed during a standard time of exposure to dry air will be thinner than that found on abraded metal not cathodically treated. Also, increase of the time allowed between abrasion and cathodic treatment will lead to the removal of more oxide, and to a thinner final film; in the limit, when all the strained metal has been oxidised before the cathodic treatment, the final film will be little liable to mechanical rupture, and will remain very thin and uniform.

In order to study the influence of different oxide-films on the subsequent behaviour of the metal immersed in chloride solutions, duplicate specimens

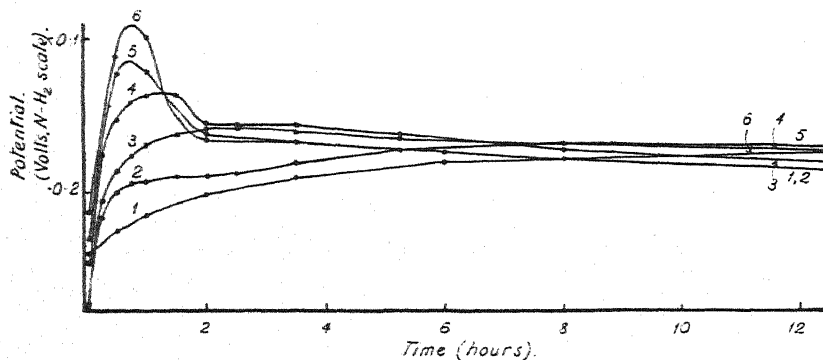


FIG. 3.—Influence of time between abrasion and cathodic treatment.

1. No treatment. 2. < 5 sec. 3. 5 min. 4. 30 min. 5. 6 hr. 6. 168 hr.

were prepared as follows. After abrasion with Hubert 1F emery-paper, specimens were stored in dry air for periods of from 1 second to 1 week, and then treated cathodically in dilute sodium carbonate for 15 seconds at a current-density of *c.* 0.05 amp./cm.². They were at once washed, dried, degreased in carbon tetrachloride, and stored in dry air for a further 72 hours before testing. In addition, a pair of specimens was abraded only and stored for 72 hours.

The corrosion experiment, with 0.1 N potassium chloride solution, was continued for 72 hours. During this time the corrosion potentials of all the specimens rose to a maximum and then fell to a nearly steady value, black spots being formed. The potential/time curves are shown in Fig. 3, and the results as a whole are summarised in Table I.

Increase of the interval allowed in the preparation of the specimens between abrasion and cathodic treatment, *i.e.*, decrease in the thickness of the pre-immersion film, is seen to lead to

- (1) decrease of the time taken to reach the breakdown state,
- (2) movement of the breakdown potential in the positive direction,

⁹ C. E. Beynon and C. J. Leadbeater, *Tech. Pub. Int. Tin. Res. and Dev. Council*, D, No. 1, 1935.

- (3) decrease of the strength of colour of the interference-tint,
- (4) more but smaller black spots.

These points are readily explained in terms of the breakdown theory developed in Section 3.

(1) If the film is originally thin and uniform, a relatively small amount of current flow between film cathode and metal/metal-oxide anode is needed to produce sufficient oxide to fill up the pores so that breakdown conditions are reached by the mechanism previously explained. The attainment of the breakdown state is therefore rapid. But if the film is originally thick, non-uniform and hence somewhat discontinuous, a relatively large amount of repair is required, and the breakdown state is only slowly reached.

(2) The less negative breakdown potentials found for the thinner films (Table I, col. 3) indicate that a greater rate of production of stannous ion is here necessary to produce breakdown. Evidently if the film is thin, breakdown is hindered by the precipitation of stannous ion as stannous hydroxide (or basic chloride) *within* the pores by the cathodically-formed hydroxyl-ion migrating inwards; while if the film is thick, the external

TABLE I.—INFLUENCE OF SURFACE CONDITION.
Means of Duplicate Experiments. Specimen Edges Unwaxed.

Time between Abrasion and Cathodic Treatment.	Thickness of Pre-Immersion Oxide-Film.	Time to Reach Break-down State.	Breakdown Potential N—H ₂ Scale.	Film after 72 Hr.*	No of Spots on Two Specimens.
		Hours.	Volts.		
(No treatment).	Decreasing ↓	29	— 0.152	YI	2
5 sec.		12	— 0.167	Weak YI	3
5 min.		2.25	— 0.159	"	2
30 min.		1.25	— 0.135	"	29
6 hr.		0.75	— 0.117	Faint YI	55 (small)
168 hr.		0.75	— 0.093	"	> 100 (v. small)

* YI indicates 1st-order yellow.

hydroxyl-ion is less well able to effect precipitation within the pores, and a smaller ratio of stannous-ion to oxide production is needed to give undermining of the film, which thus occurs at a more negative potential.

(3) The decrease in the strength of the colour of the interference-tint formed on specimens with the initially thinner films is clearly a consequence of the more rapid breakdown there found, there being in fact less time for the production of colloidal stannic oxide previously suggested; thus less film thickening occurs before black-spot formation supervenes. Any *uniform* film thickening after black-spot formation has begun will be much slower than before, since the local-action current is now mainly concentrated at the black spot, where, as explained, oxide formation is easiest.

(4) The more numerous black spots found on specimens with initially thinner films are a consequence of the more uniform nature of these films, whose pores may be expected to be much more uniform in size, and more evenly distributed, than those of the thicker, more discontinuous films. Thus breakdown conditions will be simultaneously reached at more places on specimens with thinner films than on those with thicker, with consequent increase in the number of black spots. Furthermore, since the ultimate electrode potentials of all the specimens are almost identical (Fig. 3), the cathodic process, and hence the total corrosion, must be proceeding at equal rate for all; thus when the spots are more numerous each is smaller.

The considerable differences in the behaviour of specimens abraded 5 seconds, 5 minutes and 30 minutes before cathodic treatment is noteworthy (Fig. 3, Curves 5, 4, 3). It implies that the abraded metal oxidizes rapidly between these times. Even 5 seconds oxidation, followed by cathodic treatment and a further 72 hours in dry air, seems to produce a film considerably different from that formed on a plain abraded specimen in 72 hours (Curves 5, 6). The inference is that the oxidation of tin by dry air is very rapid in the early stages. On the other hand, after 6 hours the oxide-film seems to have attained almost the same state as it has after 168 hours; in each case cathodic treatment leaves a surface which gives a very similar specimen (Curves 2, 1). Clearly, after 6 hours the rate of oxidation of abraded tin by dry air has become relatively slow. This conclusion is supported by the study of the atmospheric tarnishing of tin made by Kenworthy; ¹⁰ he has shown that the increase of weight of freshly cleaned tin specimens exposed to an indoor atmosphere is rapid for the first few hours but then becomes many times slower.

A few specimens were prepared by exposure, after abrasion, to potassium chromate solution, with a view to the repair of the original oxide-film (see Section 6). On subsequent washing and exposure to potassium chloride solution, such specimens showed higher initial potentials than untreated specimens, and the time required to reach the maximum potential was reduced; in fact, 192 hours pre-treatment in chromate produced a surface which gave the breakdown potential of -0.15 v. and the initiation of black spots immediately it was exposed to chloride. Phosphate or borate pre-treatment had a similar though less marked effect. The fact that pre-exposure to the film-repairing chromate ion has the same effects (ennoblement and production of the breakdown state) on an abraded surface as has the early exposure of such a surface to chloride solution, is further evidence of the preliminary film repair produced by chloride.

5. Influence of Chloride Concentration.

Specimens, prepared by abrasion only and 72 hours storage in dry air, were exposed under the usual conditions to potassium chloride solutions of various concentrations. For closer reproducibility all the edges of specimens were waxed. Some typical potential/time curves are shown in Figs. 4a and 4b, and the results are summarised in Table II.

TABLE II.—INFLUENCE OF CONCENTRATION OF POTASSIUM CHLORIDE.

Means of Duplicate Experiments. Specimen Edges Waxed.

Conc. KCl.	Time to Reach Breakdown State.	Breakdown Potential, N—H ₂ Scale.	Final Steady Potential, N—H ₂ Scale.
N.	Hours.	Volts.	Volts.
0.0001	>467	> + 0.096	—
0.001	225	+ 0.018	— 0.062
0.01	168	— 0.040	— 0.137
0.1	67	— 0.120*	— 0.157
0.2	62	— 0.164	— 0.182
0.4	42	— 0.191	— 0.202
1.0	18	— 0.219*	— 0.237
2.0	16	— 0.225	— 0.252
4.0	5	— 0.276	— 0.287

* Cf. Brenner's values in sodium chloride solutions, -0.11 and -0.21 v.

¹⁰ L. Kenworthy, *Trans. Faraday Soc.*, 1935, 31, 1331.

Increase of chloride concentration is seen to lead to

- (1) decrease of the time taken to reach the breakdown state,
- (2) movement of the breakdown potential in the negative direction,
- (3) movement of the final steady potential in the negative direction.

Brennert² obtained similar results, for 0.1 N and 1.0 N sodium chloride only.

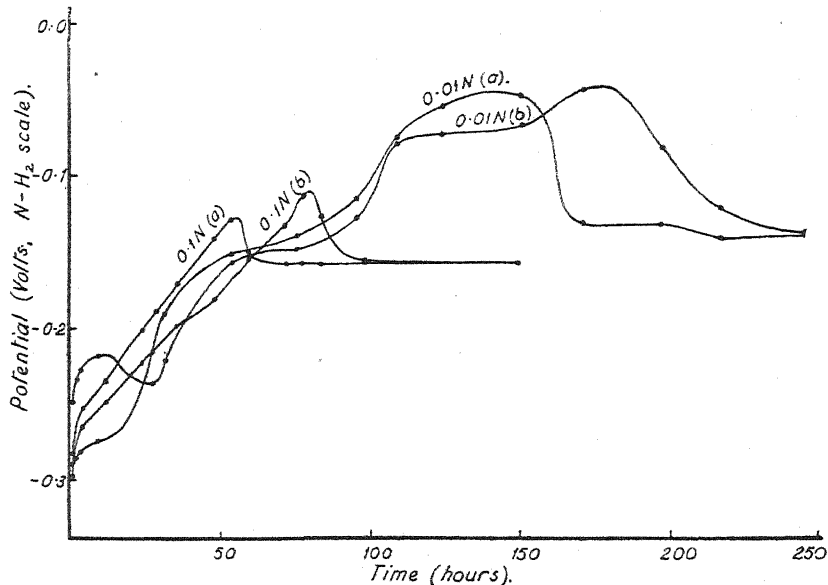


FIG. 4a.—Influence of potassium chloride concentration (dilute solutions). Both curves of duplicates shown.

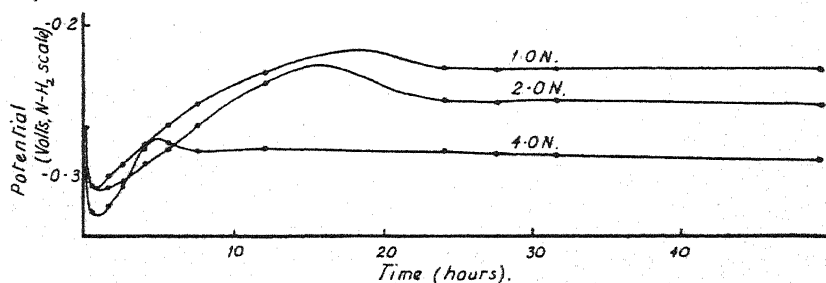


FIG. 4b.—Influence of potassium chloride concentration (strong solutions).

The theory already proposed accounts for these results as follows :

(1) Less time is taken to reach breakdown in stronger solutions because their greater conductivity allows a greater current to flow during the film-repairing process, with consequent more rapid repair.

(2) There are certainly three factors tending to make the breakdown potential more negative in concentrated solutions. Firstly, increase of electrolyte concentration decreases the electrolytic resistance of the pores in the film, and thus allows the (measured) cathodic potential to fall (in the negative direction) nearer the anodic potential, since a smaller e.m.f. is required. Secondly, complexes such as $[\text{SnCl}]^+$, SnCl_2 , $[\text{SnCl}_3]^-$ and $[\text{SnCl}_4]^{2-}$ are doubtless formed in concentrated chloride solutions,¹¹ with

consequent lowering of the stannous ion activity at the base of the pore for a given rate of tin dissolution to soluble stannous products; thus the anodic potential necessary for breakdown, and hence the measured potential, are more negative. Thirdly, increase of chloride ion concentration favours breakdown because of the well-known penetrating or peptising power of chloride ion for oxide-films; thus in presence of increased chloride, less rapid metal dissolution to soluble products is needed to produce breakdown, and the breakdown potential is more negative.

(3) The final potential obtained when black-spot formation is proceeding is no doubt made more negative by increase of chloride concentration owing to the same factors as those considered under (2), but the first factor, resistance of the electrolyte, is unlikely to have so large an influence, since the pore at a black spot is of relatively large cross-section, and the measured potential approaches close to the anodic even in dilute solution; the relatively smaller change of the final potential with chloride concentration, as compared with the change of the breakdown potential, is evidence for this view.

6. Influence of the Anion.

Specimens were prepared by the usual abrasion and stored for 240 hours or 72 hours before exposure to 0.1 M solutions of the potassium or sodium salts of many different acids. Some experiments with cathodically treated specimens were also carried out. The p_H of each solution was determined by glass electrode.

The "240-hour pre-exposure to air" experiments contain the most complete data; the potential/time curves are shown in Figs. 5, 6 and 7, and the results of 240 hours' exposure to various 0.1 M solutions are summarised in Table III. This table also shows the result of adding 0.1 M stannous chloride solution (prepared by filtering a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in water) to a sample of each solution.

It will be seen that black spot formation did not occur in solutions of those salts which give stable precipitates with "neutral" stannous chloride solution, whereas it invariably occurred in solutions which give no precipitate. This result is analogous to the non-attack of iron in chromate or phosphate solution, and of lead in sulphate, where the initial anodic product is an insoluble salt precipitated *in situ*. Evidently, in the case of tin, the conversion of a considerable proportion of the metal at the base of a pore into dissolved stannous ion, necessary for film breakdown, cannot occur in the presence of excess of a precipitating anion within the pore. The potential/time curves, Fig. 5, afford additional evidence of the protective nature of such salts, for the potential rises steadily and shows no evidence of the maximum and fall found in solutions of chlorides and other non-precipitating anions, Figs. 3, 4 and 6. The final measured potential may be far above the Sn , Sn^{++} potential, -0.136 v., for the healing of the pores by the insoluble stannous salt no doubt raises their electrolytic resistance to a very high value; thus the drop of potential between cathodic film and anodic metal becomes comparatively large.

Considerable film thickening may however occur in certain of the otherwise protective solutions. A comparison of the rate of film thickening in solutions containing the *non-oxidising precipitating anions* IO_3^- , $\text{B}_4\text{O}_7^{--}$, HPO_4^{--} , CrO_4^{--} , I^- , CNS^- , NO_2^- and HCO_3^- with the corresponding potential/time curves is of interest. The potential after 100 hours (Table III, Col. 6) may be taken as characteristic of the general "height" of the potential/time curves, and the state of the film after 240 hours (Table III, Col. 10) as indicative of the rate of film thickening. Faster film thickening is seen to be associated with a general movement of the potential/time curve in the negative direction, both effects increasing in the order of

¹¹ M. Prytz, *Z. anorg. Chem.*, 1928, 172, 147.

anions just listed. Evidently the earlier precipitates in the list are the more effective in producing film repair and thus give more rapid increase of the electrolytic resistance between the film cathode and metal anode; thus a smaller current flows, giving a slower formation of metal oxide and slower film thickening by the mechanism proposed in Section 3, while the (measured) cathodic potential, being less polarised by the smaller current, becomes more positive.

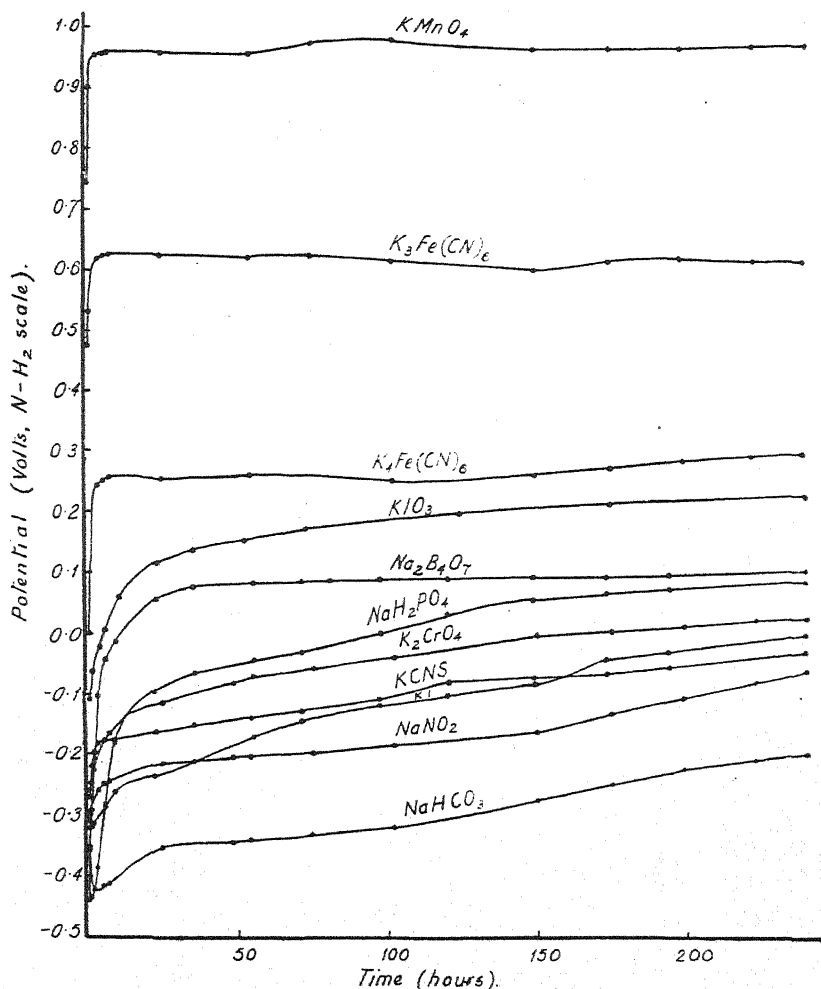


FIG. 5.—Tin-precipitating anions.

A better comparison between these solutions takes p_H into account, since a tenfold decrease in hydroxyl-ion activity should raise the cathodic potential 0.059 v. for constant current-density, if the oxygen overpotential is constant with p_H . When the potentials after 100 hours are used to calculate on these lines the potentials which should be found were all the solutions of p_H 7, the order of the anions for increasingly negative potentials is $B_4O_7^{--}$, HPO_4^{--} , IO_3^- , CrO_4^{--} , CNS^- , I^- , NO_2^- , HCO_3^- , (Table III, Col. 7). It may be noted that the only change of order introduced by the

refinement, namely the dropping of IO_3^- to third place, does not affect the argument.

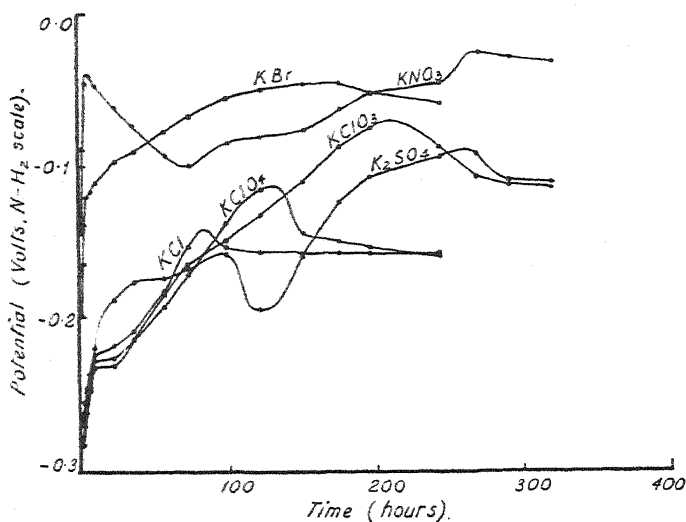


FIG. 6.—Non-precipitating anions.

The inclusion of IO_3^- and CrO_4^{2-} among the non-oxidising anions is justifiable since they fit in well with the scheme just discussed, but not with the oxidising anions next considered. The cathodic potential is

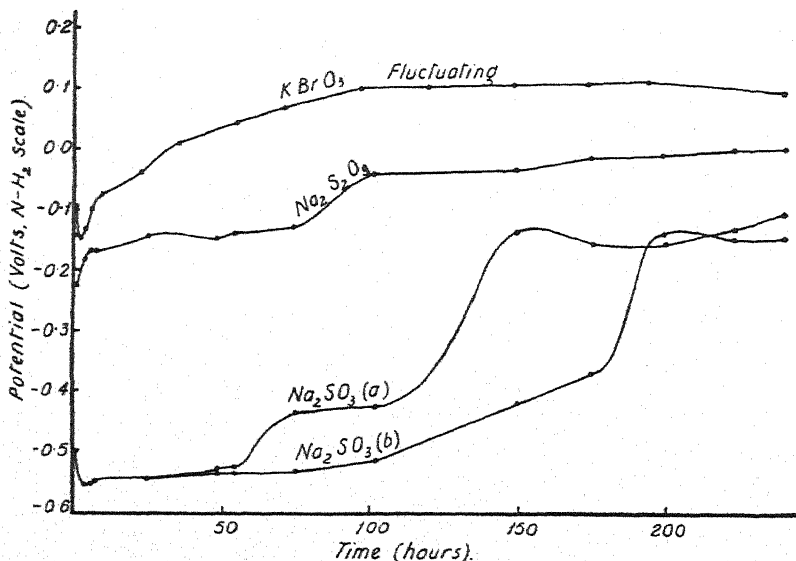


FIG. 7.—Tin-precipitating anions (unstable). Both curves of duplicates shown for Na_2SO_3 .

probably not sufficiently negative for appreciable iodate or chromate reduction to occur.

The oxidising precipitating anions MnO_4^- , $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ all gave high potential/time curves but considerable film

TABLE III.—INFLUENCE OF ANIONS AND CATIONS.

The anions are as potassium or sodium salts; the cations are as chlorides. Means of duplicate experiments. Specimen edges unwaxed. YI, MI and BI indicate 1st-order yellow, mauve and blue; the "hiatus" occurs between the 1st- and 2nd-order tints.

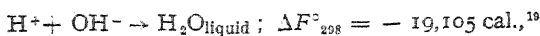
Anion.	t_H of Solution, by Glass Electrode.	Effect of Addition of Stannous Chloride Solution.	Time to Reach Breakdown State. hr.	Breakdown Potential (if any), N—H ₂ Scale.	Potential after 100 hr. (if no breakdown), N—H ₂ Scale.		Final Potential after 240 hr., N—H ₂ Scale.	Number of Points of Attack after 240 hr. on Two Specimens.	Type of Film Produced in 240 hr.
					Measured.	Calc. for t_H 7.			
			hr.	v.	v.	v.	v.		
IO ₃ ⁻	5.78	Grey ppt., pink with excess.	—	—	+ 0.188	+ 0.016	+ 0.223	0, 0	Invisible.
B ₂ O ₇ ²⁻	9.28	White ppt.	—	—	+ 0.091	+ 0.227	+ 0.098	0, 0	Invisible.
HPO ₄ ²⁻	8.61	White ppt.	—	—	+ 0.004	+ 0.101	+ 0.083	0, 0	Invisible.
CrO ₄ ²⁻	7.78	Green ppt.	—	—	— 0.038	+ 0.008	+ 0.024	0, 0	Trace YI.
CNS ⁻	6.36	White ppt. formed slowly.	—	—	— 0.105	— 0.143	— 0.036	0, 0	YI-MI.
I ⁻	6.49	Yellowish ppt.	—	—	— 0.115	— 0.145	+ 0.003	0, 0	YI-MI-BI.
NO ₃ ⁻	6.63	White ppt., NO ₂ evolved.	—	—	— 0.182	— 0.204	— 0.067	0, 0	YI-MI-BI.
HCO ₃ ⁻	8.50	White ppt., CO ₂ evolved.	—	—	— 0.322	— 0.233	— 0.204	0, 0	MI—"Hiatus."
MnO ₄ ⁻	7.54	Brown ppt.	—	—	+ 0.080	—	+ 0.980	0, 0	MI.
Fe(CN) ₆ ⁴⁻	6.28	Whitish-blue ppt.	—	—	+ 0.623	—	+ 0.623	0, 0	YI-MI.
Fe(CN) ₆ ³⁻	8.45	Whitish-blue ppt.	—	—	+ 0.253	—	+ 0.293	0, 0	YI-MI.
SO ₃ ²⁻	7.84	White ppt.	—	—	— 0.316	— 0.467	— 0.48*	0, 0*	Invisible.*
Cl ⁻	6.07	No ppt.	80	— 0.142	—	—	— 0.157	14, 11	YI-MI.
Br ⁻	6.65	No ppt.	160	— 0.042	—	—	— 0.059	2, 4	YI-MI.
ClO ₃ ⁻	6.41	No ppt.	210	— 0.074	—	—	— 0.116	1, 1 (deep).	YI-MI.
ClO ₄ ⁻	6.06	No ppt.	120	— 0.116	—	—	— 0.155	1, 1 (small).	YI-MI.
SO ₄ ²⁻	6.06	No ppt.	250	— 0.094	—	—	— 0.112	1, 1	YI-MI.
NO ₂ ⁻	6.19	No ppt.	260	— 0.027	—	—	— 0.037	6, 3 (v. small).	YI-MI.
BrO ₃ ⁻	6.04	White ppt., turning brown.	100	+ 0.100	—	—	+ 0.088	4, 9	Weak YI.
S ₂ O ₃ ²⁻	7.67	White ppt., turning yellow.	—	—	— 0.038	+ 0.001	— 0.001	0, 0	MI—"Hiatus."
NH ₄ ⁺	5.26	No ppt.	80	— 0.155	—	—	— 0.159	5, 14 (large).	YI-MI-BI.
Mg ⁺⁺	5.91	No ppt.	64	— 0.103	—	—	— 0.182	5, 1	YI-MI.
Ca ⁺⁺	5.56	No ppt.	62	— 0.107	—	—	— 0.186	3, 4	YI-MI.
Zn ⁺⁺	6.00	No ppt.	60	— 0.155	—	—	— 0.159	65, 65 (v. large).	Trace YI.

* After 120 hr.; see text.

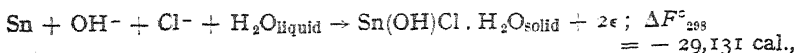
Thus since



and



we have



or a standard potential for the Sn, Sn(OH)Cl · H₂O, $\left\{ \begin{array}{l} \text{OH}^{-} \\ \text{Cl}^{-} \end{array} \right.$ electrode of -0.631 v. The variation of the potential of this electrode with p_{H} in 0.1 M potassium chloride solution where the chloride-ion activity²⁰ is c. 0.076 N, is shown by line 3 of Fig. 8. Evidently the anodic formation

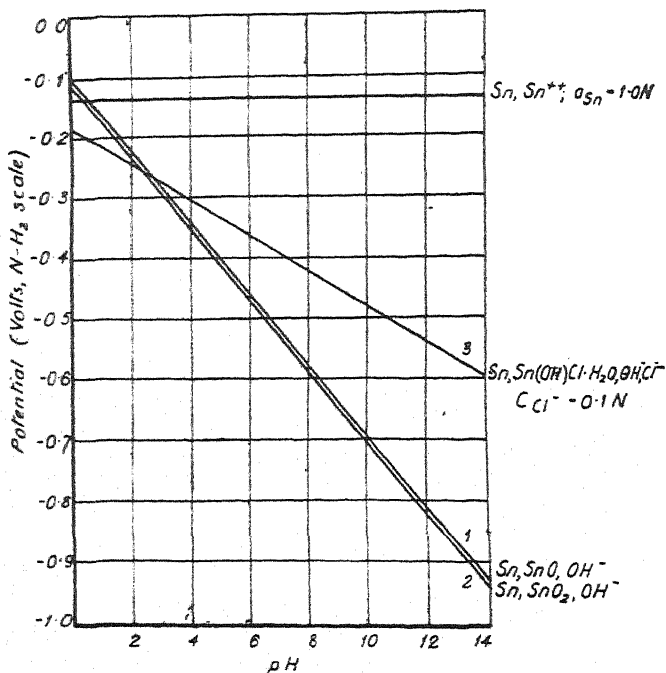


FIG. 8.—Theoretical potentials.

of Sn(OH)Cl · H₂O will tend to take place preferentially to that of either oxide at a $p_{\text{H}} < c. 2.5$ and potentials more positive than c. -0.25 v. Thus the film-repairing process in chloride solution probably involves the precipitation of basic chloride as well as the oxides.

The anodic formation of stannic ion is unlikely, except in oxidising solutions. The standard potential of the Sn, Sn⁺⁺⁺⁺ electrode may be obtained from that of the Sn, Sn⁺⁺ electrode and that of the Sn⁺⁺, Sn⁺⁺⁺⁺ oxidation-reduction process,²¹ being $\frac{1}{2}(-0.136 + 0.154) = +0.009$ v. This is much more positive than the potential of the Sn, Sn⁺⁺ electrode, and it thus appears that stannic ion could be formed only in strongly oxidising solutions giving high positive potentials.

¹⁹ G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill), 1923, p. 486.

²⁰ G. Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 648; H. S. Harned, *J. Amer. Chem. Soc.*, 1929, **51**, 416; T. Shedlovsky and D. A. MacInnes, *J. Amer. Chem. Soc.*, 1937, **59**, 593.

²¹ C. S. Huey and H. V. Tartar, *J. Amer. Chem. Soc.*, 1934, **56**, 2584.

10. Summary.

The attack of tin by solutions of the alkali metal salts of many anions, and of the chlorides of a few cations, has been studied electrochemically. Repair of the pre-immersion film takes place first owing to anodic oxide formation within its pores, but when the anodic metal at the base of the pores becomes sufficiently polarised, due to deficiency of hydroxyl ion, a sufficient proportion of soluble stannous ion may be formed there to give undermining and breakdown of the film. The consequent increased anodic oxide-formation then produces a black spot at the point of breakdown. Black spots are formed on tin by salt solutions which give no precipitate with stannous ions (chloride, bromide, chlorate, perchlorate, sulphate and nitrate), but not by solutions giving stable precipitates (iodate, borate, mono-hydrogen phosphate, chromate, thiocyanate, iodide, nitrite, bicarbonate, permanganate, ferricyanide, ferrocyanide and sulphite), since here undermining cannot occur; of the anions studied, chlorides give the most attack. Concentrated chloride solutions give more rapid breakdown than dilute. Ammonium, magnesium, calcium and zinc chloride solutions behave similarly to potassium and sodium, except that black spots, once formed, grow faster.

Indirect evidence that the rate of oxidation of freshly abraded tin is very rapid for the first few minutes, but becomes relatively very slow after about six hours, has been obtained.

This work has been carried out for the International Tin Research and Development Council, and my thanks are due to Mr. D. J. Macnaughtan, Director of Research, for valuable comments and permission to publish. I am much indebted to Dr. U. R. Evans and to Mr. O. Gatty for some stimulating discussions, and to my assistant, Mr. G. E. S. Eyles, for his very careful preparation of the experimental materials.

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SURFACE TENSION AND VISCOSITY PHENOMENA IN TINPLATE MANUFACTURE.

BY BRUCE CHALMERS.

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I. Introduction.

The manufacture of tinplate can be divided into three distinct stages: (a) the metallurgical processes of preparing the steel sheets, (b) the chemical stages of pickling and fluxing, and (c) the physical operations of coating the steel sheet with tin. It is with the third section that the present paper deals.

The operations of coating the prepared steel sheet with tin which are to be considered are as follows: The steel sheet passes upwards from the molten tin in the tinpot into the palm oil above it, through the grease pot rolls, and soon after leaving the grease pot the tin solidifies, after which no further fundamental changes take place. The value of the final product depends on the amount and distribution of the tin on

the sheet after solidification; and since the process of freezing involves a contraction of only 2 per cent., it follows that the characteristics of the solid surface will follow closely those of the liquid surface just before solidification. The factors that influence the characteristics of the surface of the liquid tin on the steel sheet are dealt with below.

As the steel sheet passes upwards through the grease pot rolls, a large part of the tin adhering to the sheet is squeezed off. That this must be so is shown in Section III., in which it is proved, as is known in practice, that, but for the grease pot rolls, the tin yield would be far greater than it is.

In Section III. it is shown that the time elapsing after the sheet has left the rolls and before solidification is too small for any important change of distribution to take place, except for the two "local" effects, responsible for the production of normal and potential pores,^{1, 2} which are described in Sections II. and IV. respectively.

II. Normal Pores.

A normal pore in tinplate is described by Hoare^{1, 2} as consisting of a roughly circular surface of exposed steel surrounded by a ring of the

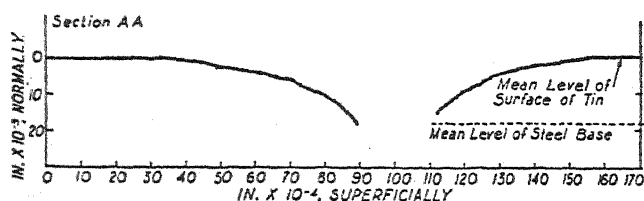


FIG. 1.

iron-tin compound, FeSn_2 . Examination by the interference fringe method³ indicates that the cross-section through the centre of such a pore has the shape represented in Fig. 1. The presence of such a pore in the solid tin coating depends upon the stability of a liquid surface of the same shape, and the surface tension conditions governing this stability are now considered.

When a suitably prepared steel base is dipped into molten tin, the tin reacts with the steel and forms a layer of compound to which the tin tends to adhere when the steel is withdrawn from the tin bath. In the case of copper, the tin sometimes tends to adhere to the copper tin compound layer forming a smooth coating; but under different conditions it tends to retract into restricted regions ("dewet"), giving an irregular coating. The latter case need not be considered further here as the chief cause of porosity is then not the normal pores but the "dewetted" part of the surface. In other cases copper and steel behave similarly.

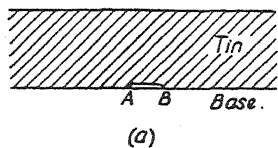
Suppose that on the surface of the steel or copper base, there is a region where the reaction does not occur, such as AB in Fig. 2(a). The

¹ W. E. Hoare, *J. Iron and Steel Inst.*, 1934, **129**, 253; *Tech. Publ. International Tin Research and Development Council*, Series A, No. 2, 1935.

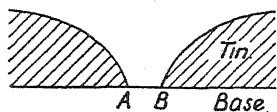
² W. E. Hoare, *Proc. Swansea Tech. Coll. Met. Soc.*, December, 1934; *Tech. Publ. International Tin Research and Development Council*, A. 14.

³ W. E. Hoare and B. Chalmers, *J. Iron and Steel Inst.*, 1935, **132**, 135; *Tech. Publ. International Tin Research and Development Council*, A, 21, 1935.

tin at this region does not tend to adhere to the base, so that a tin surface is left in contact with the non-reactive region of the base. This increases the total area of tin surface, which may be reduced by the formation of a pore as in Fig. 2(b). The latter can only happen when the total area of surface is less when a pore is formed than when it is not.



(a)



(b)

FIG. 2.

When a surface subject to surface tension has a curved form, the surface tension forces may be such as to cause a pressure difference between the two media separated by the surface; this excess pressure P at any point is given by $P = T(1/R_1 + 1/R_2)$ where T is the surface tension and R_1 and R_2 are the principal radii of curvature at the point considered.

If the surface is in equilibrium, the excess pressure P must be the same for all points of the surface. In the case of a surface such as that of Fig. 2(a), a point can be found where the surface is plane; at such a point $1/R_1$ and $1/R_2$ are both zero, hence $1/R_1 + 1/R_2 = 0$ for any point on the surface.

The surface which satisfies these conditions is the catenoid; this can be treated mathematically* and a plane central section is such that

$$x = x_0 \cosh y/x_0 \quad . \quad . \quad . \quad (i)$$

which is represented in Fig. 3. The area of the figure of rotation of such a figure bounded by planes $y = 0$ and $y = l$ is

$$s = \pi a^2 (\sinh n \cosh n + n) / \cosh^2 n \quad . \quad . \quad (ii)$$

where $n = l/x_0$.

For the present purpose the figure must be regarded as bounded at the top by the plane to which the figure is asymptotic, and at the bottom by any other plane which may be chosen. It is required to calculate whether the area of the catenoid between these limits is greater or less than the sum of

the areas of the circles of contact in the two bounding planes. It is necessary to approximate as far as the upper bounding plane is

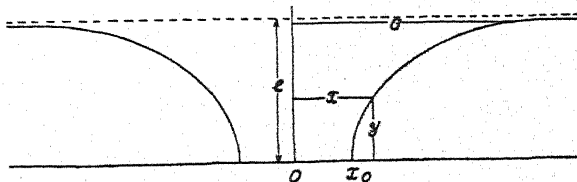


FIG. 3.

concerned, since the radius of the circle of contact is infinite. If the plane ($l = 10x_0$) be chosen, it can be shown from equation (i) that $a = 10000x_0$, and the error introduced by substituting this plane for the actual limiting plane is small. If S_1 is the area of the catenoid between $y = 0, x_0, 2x_0$, etc., and $y = 10x_0$, and S_2 is the sum of the areas of the circles intersecting the catenoid at $y_0 = 0, x_0, 2x_0$, etc., and $y = 10x_0$, then the values shown in table on page 1171 are found.

* See G. F. C. Searle, *Experimental Physics*, C.U.P., 1934, p. 143.

In the third column a correction Δ is added for the part of the figure, neglected above, which lies between $y = 10x_0$ and $y = 12x_0$, at which plane the radius is 156,600. The further correction beyond this point is negligible.

When the value of $S_1 - S_2 + \Delta$ is positive, the area of the catenoid is greater than the sum of the areas of the two circles, or the total surface area is increased by the replacement of the flat continuous film (1a) by the catenoid film (1b), and vice versa.

The figures given in the table are plotted in Fig. 4, from which it follows that $S_1 - S_2 + \Delta = 0$ when $y = 1.7x_0$. At this point $a = 2.6x_0$. Hence the limit of stability is when the lower bounding circle has a diameter of $5.2x_0$ and is situated at a depth of $7.4x_0$ below the surface $y = 10x_0$. Hence the minimum diameter of a non-reactive region which can cause a pore is $5.2/7.4$ of the thickness of the coating, i.e., the dia-

y .	$S_1 - S_2$.	$S_1 - S_2 + \Delta$.
0	$14 \pi x^2$	$19 \pi x^2$
x_0	$10 \pi x^2$	$15 \pi x^2$
$2x_0$	$-15 \pi x^2$	$-10 \pi x^2$
$3x_0$	$-190 \pi x^2$	$-185 \pi x^2$
$4x_0$	$-1502 \pi x^2$	$-1497 \pi x^2$
etc.	etc.	etc.

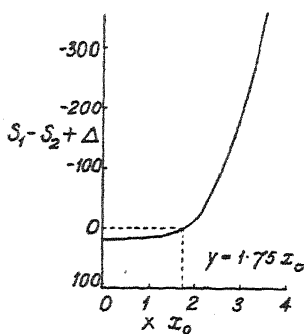


FIG. 4.

meter of the base of a pore must be at least 0.7 of the thickness of the coating.

This calculation shows that the only criterion as to whether a pore is stable or not is the ratio of the diameter of the "non-reactive region" (assumed to be circular) to the thickness of the coating, and that unless the diameter is greater than 0.7 of the thickness of the coating, the pore is unstable, while for diameters exceeding this value the stability increases rapidly (see Fig. 4). The fact that a pore formed on a non-reactive area of more than this size would be stable does not mean necessarily that such a pore would form, since the coating is originally continuous and of the type indicated in Fig. 2(a) as it leaves the tin bath. It is then necessary therefore to consider the mechanism that operates when a pore is formed.

During the time that elapses between the withdrawal of the steel sheet from the tin bath via the grease pot, and the solidification of the tin, both grease and tin are continuously draining from the surface under the influence of gravity. The draining of the grease will be discussed in the next section, and we will for the moment consider the period after the greater part of the grease has drained and before the tin solidifies. The tin tends to drain under gravity, and opposing this is the adhesion of the tin to the compound layer which is wetted by it. The viscosity of the tin also tends to retard its drainage. At non-reactive regions the adhesion is zero, so the tin drains off these regions more quickly than elsewhere, tending to leave a bare patch wherever there is a non-reactive region. This bare patch will only be stable if, as pointed out above, the diameter is greater than about 0.7 of the thickness of the coating. Since the thickness of the tin coating is

continuously diminishing during the above process, the tendency to form pores increases until the tin solidifies; hence most of the pores will be formed comparatively late in the process.

It is evident that in practice the non-reactive areas will not usually be circular and that the foregoing analysis cannot therefore apply exactly; in such cases the calculation becomes much more complicated because the surface is no longer a surface of revolution. It is clear, however, that for a nearly circular region the result will be similar, the diameter being replaced by some other length, possibly the mean of the smallest and largest axes of the figure.

It is concluded, then, that unless the size, *i.e.*, effective radius of a non-reactive region is greater than about 0.7 of the local thickness of the tin coating, a normal pore cannot be formed.

III. Movement of Tin under Gravity before Solidification.

The effect of gravity in altering the distribution of the molten tin on the base after passing through the grease pot rolls and before solidification will now be considered.* It will be assumed that the compound layer is smooth and that the tin immediately in contact with it is at rest relatively to it; any irregularities of the compound layer of small depth compared with that of the liquid layer will have little influence on the result, and the assumption of no relative movement is justified by the fact that the tin wets the compound layer. (This would not necessarily hold for hot-tinned copper.)

The tin layer on the steel base is acted upon by two forces. (1) The weight of the tin, downwards; (2) the viscosity opposing motion of the tin. When these two forces are equal the tin will have attained a constant velocity. This constant or terminal velocity will now be calculated.

Let the tin layer be uniform and of thickness x , and let it be divided into elementary laminæ of thickness δx . Consider an area of 1 cm.² of such a lamina; the forces on this lamina are:

(1) Gravity = $\rho g \delta x$ downward.

(2) Viscosity = $\eta \frac{dv}{dx}$ at each surface of the lamina, upward at one surface and downward at the other, v being the vertical velocity; if the downward direction is regarded as positive, the total force is:

$$\begin{aligned} & -\eta \frac{d}{dx} \cdot \frac{dv}{dx} \cdot \delta x \\ & = -\eta \frac{d^2v}{dx^2} \cdot \delta x. \end{aligned}$$

When the terminal velocity v_t has been attained, the two forces are equal, when

$$\rho g \delta x = -\eta \frac{d^2v}{dx^2} \cdot \delta x,$$

or
$$\frac{d^2v}{dx^2} = -\frac{\rho g}{\eta} = \text{a constant, } (-K),$$

$$\therefore v_t = -\frac{Kx^2}{2} - Ax - B.$$

* A related problem has been discussed by H. Jeffreys, *Proc. Camb. Phil. Soc.*, 1930, 26, 204-205.

The boundary conditions are :

(1) at $x = 0$, $v = 0$; whence $B = 0$.

(2) the weight of tin between any given plane x' and the boundary $x = X$ is equal to the viscous force on that plane or

$$\rho g'(X - x') = \eta \frac{dv}{dx} \Big|_{x'},$$

or
$$\rho g'(X - x) = \eta \frac{dv}{dx},$$

whence
$$\frac{dv}{dx} = K(X - x) = KX - Kx,$$

but
$$\frac{dv}{dx} = Kx - A, \quad \therefore A = -Kx,$$

$$\therefore v_t = -\frac{Kx^2}{2} + KXx.$$

The maximum velocity is at the outside plane $x = X$ where

$$v_t(\text{max.}) = -\frac{KX^2}{2} + KX^2 = \frac{KX^2}{2},$$

$$\therefore v_x = \frac{\rho g' X^2}{2\eta},$$

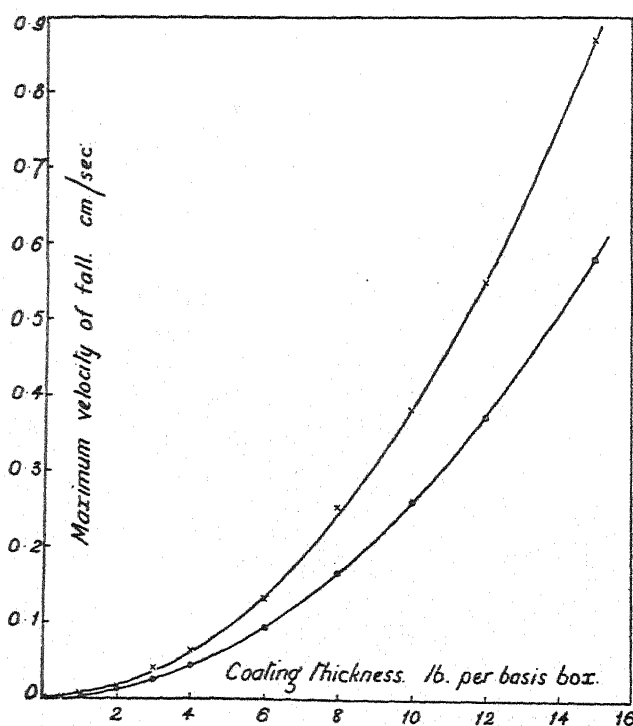


FIG. 5.

from which numerical values can be computed. The value of K varies from 5.53 at 240°C. to 5.61 at 300°C. ; hence the effect of temperature is small and can be neglected. The graph (Fig. 5) shows the maximum

velocity of the outer layer in terms of the thickness of the tin layer x ; this thickness being expressed in pounds per basis box.*

It will be observed that, owing to the small values of x found in practice, the velocities are small, the value for 15 lb./basis box being less than 1 cm./sec.; when the outer layer is moving at this speed, the mean velocity of the coating is equal to $KX^2/3$, and therefore equal to two-thirds of the maximum value; the values for the mean speed of descent are shown on the same graph (lower curve).

The conclusion is that the movement of the tin under gravity on the base is very small after the tin has been distributed by the grease pot rolls.

IV. Grease Marks.

When the tinned sheet leaves the rolls, it passes through a meniscus, or nip of palm oil, tending to carry a layer of oil upwards with it, the oil meanwhile tending to drain downward under the influence of gravity. Most of the grease drains back into the nip at once, a thin layer only being carried upwards on the sheet; this layer becoming progressively thinner upwards. Hence the conditions are those of a thin layer of oil resting on the tin layer which is also liquid.

It has been shown by Hardy⁴ that when a layer of one liquid rests on another liquid, the upper layer may be unstable and break up into drops. The tendency to do so increases as the thickness of the upper liquid layer decreases, instability being reached when the thickness decreases to a definite value. The experiments of Hardy apply to the case of a horizontal film on a horizontal liquid layer, but the less usual case of a vertical film on a vertical liquid surface does not seem to have been adequately investigated. The conditions studied by Hardy would then be modified by the influence of gravity, and it is evident that the breaking up of the film into drops is considerably modified by the action of gravity since a drop once formed would tend to move downwards, instead of remaining stationary.

The following mechanism is suggested for the breakdown of the grease film. Let the line PQ in the diagram, Fig. 6, represent the region of the sheet of tinplate where the oil film reaches the critical thinness and becomes unstable. Any irregularity (such as may result from variation in thickness of the underlying tin layer) may cause grease to collect at a point such as A and to leave the surroundings. Such drops will tend to form on the thickest parts of the tin layer, leaving more grease on these parts than at other places, because such drops will have less surface tension energy associated with them when they do not completely penetrate the tin than when they do. This aspect is referred to again in connection with the final form of the grease marks. When the drops are of sufficient size, they will run downwards forming continuous runnels, which will be continuously replenished by the same process. The grease composing a runnel drains downwards by gravity and eventually a stage is reached, as the sheet moves upwards, when the strip of grease which the runnel leaves on the tin is unstable and

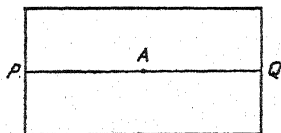


FIG. 6.

* 1 lb. per basis box is equivalent to 0.00015 cm.

⁴ W. B. Hardy, *Proc. Roy. Soc., A*, 86, 1912, 610-635.

splits up into drops. Thus in the stable state of affairs all the grease which does not at once drain and so remain in the "nip," is later collected into equidistant runnels, which themselves break up into drops, as they drain. The process is therefore the process of drop formation divided into two stages, the first, or linear, being caused by gravity, and hence not appearing in the "horizontal" case.

When the drops have formed, they will be carried upwards until the tin freezes, the drops being of such size that their weight is insufficient to cause them to drain.

Potential pores are caused by the presence of such drops on the tin surface when it solidifies, and it can be shown that their shape is similar to that which would be expected from a consideration of surface tension forces. A drop of a liquid A on a liquid surface B can be stable only if the excess pressure in A due to surface tension is constant at every point of the surface (apart from a very small correction for gravity),

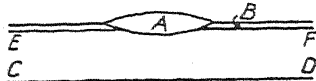


FIG. 7.

and if the surface energy is a minimum; these two conditions are satisfied only if each surface of the drop is spherical in shape. The curvatures of the two surfaces need not be the same. The lower surface will therefore be a spherical arc if the liquid B extends downwards for a sufficient depth (e.g., to CD) or a portion of a sphere lying between two parallel planes if the depth is less (e.g., EF, Fig. 7). The latter is the case shown in Fig. 3, of Hoare and Chalmers.³ In the latter case (i.e., that in which the depth of the coating is less than the depth of the complete drop), a further consideration appears, depending on the surface tension of tin and grease and their interfacial tensions with FeSn_2 . Two distinct cases must be considered (a) that in which a layer of oil covers the tin and (b) in which drops of oil exist on the tin surface. The two cases are illustrated in Fig. 8. The oil will spread, in case (a), if $T_1 + T_3 > T_4$ and, in case (b) if $T_3 + T_5 > T_2 + T_4$.

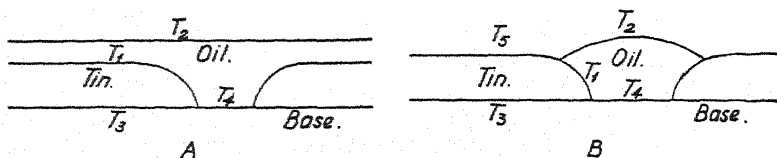


FIG. 8.

It is clear from the fact that grease cups do not spread to expose large areas of compound that the condition B is not satisfied; hence T_4 is large and the arc of contact of oil drop and compound tends to a minimum. Thus the drops will tend to migrate towards those parts where the tin layer is thickest.

Measurements of the profiles of such drops have been made by examining the interference fringes with a microscope and viewing a scale simultaneously by means of an inclined glass plate just above the eyepiece; the apparent positions of the fringes were observed on the scale. The magnification was determined by applying the same process to a finely divided scale, and was about one thousand. The depth represented by a fringe being known, and their lateral distances having thus been measured, it was possible to plot the profile of any grease spot

or other pore. A number of such profiles were plotted, a typical example being given in Fig. 9, in which an arc of a circle is also shown. It will be seen that the agreement is good, indicating that the shape of the hollow is consistent with its formation by the surface tension associated with a drop. Any other cause, such as excessive drainage during solidification delayed by the presence of the grease, would be expected to

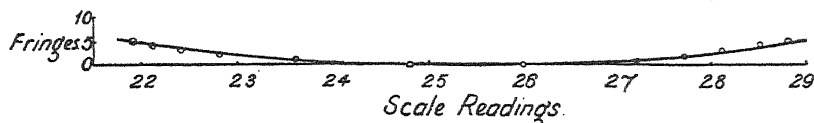


FIG. 9.

cause hollows less regular in shape and showing some discrimination between the horizontal and the vertical directions. Such a process may account for the parts of the grease lines between the cups, these parts consisting usually of pronounced furrows in the tin.

“Half Loops.”

It will be observed that in Section II. the formation of normal pores was considered without reference to the oil layer, the normal pores being formed after the drainage of the oil. It is obvious, however, that some normal pores may be formed before the oil has run into lines, and that such pores will be different from those considered. A pore forming while there is still a mobile layer of oil on the surface will tend to act as a site for the formation of a drop of oil, since this would reduce the surface energy of both; hence a normal pore may cause a grease cup to be formed off the grease lines; such a pore must, on account of its early appearance, be a large one.

If, on the other hand, a pore forms after the segregation of the grease into lines but before the lines break down into drops, the normal pore may, owing to the modification of the surface in its neighbourhood, draw a drop of oil from the line to the site of the pore. The modification of the surface form due to a normal pore would be appreciable at a distance from the pore of at least 1000 times the thickness of the coating, and so any pore forming within this distance of the grease line may deflect the line or draw a drop from it. It has been observed that when a drop of oil on tin travels across the surface, it leaves a pair of lines *a, a*, as in Fig. 10, which illustrates diagrammatically the formation of a half-loop.

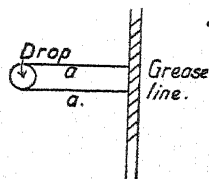


FIG. 10.

The formation of such lines is always associated with the movement of a grease drop, and may frequently be observed near the front edge of a sheet where large drops of grease have been carried up before the grease lines have established themselves, and have subsequently run down a short distance before the solidification of the tin. The lines marking the path of the drop have been shown by means of interference fringes to be grooves.

Summary.

The following applications of surface tension and viscosity theory to the hot dipping process in the manufacture of tinplate are discussed:—

(1) The appearance of normal pores in terms of the stability of the catenoid film.

(2) The appearance of potential pores and grease lines in terms of the theory of the stability of one liquid film on another.

(3) The rate of draining of liquid tin under gravity in terms of viscosity.

The author wishes to express his indebtedness to the International Tin Research and Development Council for a grant, and to its Director, Mr. D. J. Macnaughtan, F.Inst.P., for his encouraging interest in this work. Acknowledgment is made to the Governors and Principal of the Sir John Cass Technical Institute for facilities. Thanks are also due to Mr. W. E. Hoare, B.Sc., for helpful discussions and valuable suggestions during the course of this investigation. Fig. 1 is reproduced by courtesy of the Council of the Iron and Steel Institute.

The Sir John Cass Technical Institute.

THE EFFECT OF AMINO-ACIDS ON THE SURFACE TENSIONS OF SODIUM CHLORIDE SOLUTIONS.

By J. W. BELTON.

Received 17th March, 1937.

The surface tensions of solutions of amino-acids are of interest in that the acid may be present largely as undissociated molecules, when a decrease in surface tension with acid concentration, as for acetic acid, would be expected, or as zwitterions, when the surface tension should increase and water be positively adsorbed at the surface, as is found for most electrolytes. In the case of glycine, for example, the surface tension increases, indicating the presence of zwitterions in its solutions. The effect of slightly soluble amino-acids, the surface tensions of solutions of which are very little different from that of water, is much more marked in concentrated salt solutions, and in order to investigate the behaviour of aspartic acid, asparagine, glutamic acid, *o*-amino benzoic, *m*-amino benzoic and *p*-amino benzoic acids, the surface tensions of their saturated solutions in the presence of varying concentrations of sodium chloride have been measured.

Experimental.

The surface tensions were measured by the modification of the maximum bubble pressure method previously described.¹ The jet used in this investigation was 0.01214 cms. radius; it gave 72.01 dynes/cm. for the surface tension of water, and 28.20 dynes/cm. for that of benzene, values which agreed with those obtained previously with other jets. All measurements were made at 25° C.

The ternary solutions were made up from stock solutions of sodium chloride of analar grade containing one, two, three and four moles per litre, respectively. The surface tensions of these solutions agreed with those previously determined.² The water used had a surface tension of 72.01

¹ Belton, *Trans. Faraday Soc.*, 1937, **33**, 440.

² *Ibid.*, 1935, **31**, 1413.

dynes/cm. The amino-acids were estimated by titration or by the determination of nitrogen with the following results: aspartic acid, 97.2 per cent., with a trace of ammonium chloride; asparagine, 99.9 per cent.; glutamic acid, 99.2 per cent.; *o*-amino benzoic acid, 99.3 per cent., m.p. 147°; *m*-amino benzoic acid, 100 per cent., m.p. 172°; *p*-amino benzoic acid, 98.6 per cent., m.p. 184°.

TABLE I.

m_1	h	γ	$\Delta\gamma$	k
<i>Aspartic Acid</i>				
—	11.605	72.09	—	—
1.022	11.88	73.81	1.72	1.68
2.100	12.15	75.48	3.39	1.61
3.194	12.43	77.22	5.13	1.61
4.365	12.74	79.15	7.06	1.62
				Mean 1.63
<i>Asparagine</i>				
—	11.66	72.42	—	—
1.022	11.925	74.06	1.64	1.60
2.100	12.195	75.75	3.33	1.59
3.194	12.485	77.56	5.14	1.61
4.365	12.74	79.15	6.73	1.55
				Mean 1.59
<i>Glutamic Acid</i>				
—	11.62	72.18	—	—
1.022	11.86	73.67	1.49	1.46
2.100	12.14	75.41	3.23	1.54
3.194	12.415	77.13	4.95	1.55
4.365	12.685	78.79	6.61	1.52
				Mean 1.52
<i>o</i> -Amino Benzoic Acid				
—	11.37	70.63	—	—
1.022	11.585	71.96	1.33	1.30
2.022	11.79	73.23	2.60	1.24
3.194	12.00	74.54	3.91	1.22
4.365	12.20	75.79	5.16	1.18
				Mean 1.23
<i>m</i> -Amino Benzoic Acid				
—	11.60	72.06	—	—
1.022	11.80	73.30	1.24	1.21
2.100	12.01	74.59	2.53	1.20
3.194	12.26	76.16	4.10	1.28
4.365	12.54	77.89	5.83	1.33
				Mean 1.25
<i>p</i> -Amino Benzoic Acid				
—	11.55	71.75	—	—
1.022	11.815	73.38	1.63	1.59
2.100	12.04	74.79	3.04	1.45
3.194	12.285	76.32	4.57	1.43
4.365	12.59	78.20	6.45	1.48
				Mean 1.49

$$\gamma - \gamma_0 = km_1$$

where γ_0 is the surface tension of water and k is a constant. Similar constants ($\Delta\gamma/m_1$) have been calculated for the ternary solutions and are given in the final column of the Table. There is a linear relationship in each case between the surface tension of the ternary solution and the salt concentration. The surface tensions of the

saturated amino-acid solutions in water are very little different from that of water itself, those of asparagine and glutamic acid being slightly higher, and those of aspartic acid, *o*- and *p*-amino benzoic slightly less. The divergence, however, between the surface tensions of the ternary solutions and those of the corresponding salt solutions becomes greater with in-

creasing concentration of salt. Thus the presence of the acid, which has very little effect on the surface tension of water, has a comparatively large effect on the surface tension of a strong salt solution. The surface tension increment for the mixture is not equal to the sum of the increments each solute would produce if present separately. A similar behaviour was found for mixtures containing salt and dilute hydrochloric acid. The γ - m curves for solutions containing amino-acid lie in all cases below that for pure sodium chloride solutions.

The Adsorption of Water.

The difficulties in the calculation of the adsorptions of the components at the surface of ternary solutions have been previously pointed out by the writer¹ who has shown that in certain cases they may be obtained. In a mixture containing an electrolyte and a non-electrolyte, the calculations are simplified if the solution remains saturated with respect to the latter while the concentration of the former is varied; in this way the surface structure of such solutions may be investigated. This method may be applied to find the effect of amino-acids on the adsorption of water at the surface of solutions containing sodium chloride.

From the standpoint of the classical theory of amino-acids there may be present in the solution the two ions derived from the acid, hydrogen ions and hydroxyl ions, as well as the undissociated portion of the acid; further, it is possible that a large fraction of the latter is present in the form of zwitterions. The Gibbs equation for such a system is

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3$$

where Γ_1 , Γ_2 , Γ_3 and μ_1 , μ_2 , μ_3 refer to the surface concentrations and chemical potentials of sodium chloride, water and amino-acid respectively. The value of k for any amino-acid is thus given by

$$\left(\frac{\partial\gamma}{\partial m_1}\right)_{\mu_2, \mu_3} = -\Gamma_1 \left(\frac{\partial\mu_1}{\partial m_1}\right)_{\mu_2, \mu_3} - \Gamma_2 \left(\frac{\partial\mu_2}{\partial m_1}\right)_{\mu_2, \mu_3} - \Gamma_3 \left(\frac{\partial\mu_3}{\partial m_1}\right)_{\mu_2, \mu_3} \quad (1)$$

As the addition of sodium chloride to water increases its surface tension, the dividing surface may be drawn so that the surface concentration of salt is zero. In the solutions investigated here, the undissociated portion of the amino-acid is in equilibrium with the solid form, and consequently its chemical potential must be constant; and further, from a consideration of the ionic equilibria involved, it follows that the sum of the chemical potentials of the ions present is constant, and also their individual values. If the acid is present as zwitterions, then these are in equilibrium with the solid and must be at constant chemical potential. Thus equation (1) reduces to

$$\left(\frac{\partial\gamma}{\partial m_1}\right)_{\mu_2, \mu_3} = -\Gamma_2 \left(\frac{\partial\mu_2}{\partial m_1}\right)_{\mu_2, \mu_3} \quad (2)$$

Combining this with the Duhem-Margules equation,

$$\sum n d\mu = 0$$

we obtain

$$\begin{aligned} \left(\frac{\partial\gamma}{\partial m_1}\right)_{\mu_2, \mu_3} &= \Gamma_2 \frac{n_1}{n_2} \left(\frac{\partial\mu_1}{\partial m_1}\right)_{\mu_2, \mu_3} \\ &= \Gamma_2 \frac{n_1}{n_2} RT \left(\frac{\partial \log f_{\pm} m_1}{\partial m_1}\right)_{\mu_2, \mu_3} \\ &= \Gamma_2 \frac{n_1}{n_2} RT \left\{ \frac{1}{m} + \left(\frac{\partial \log f_{\pm}}{\partial m_1}\right)_{\mu_2, \mu_3} \right\} \quad (3) \end{aligned}$$

The surface concentration of water may thus be calculated from the slope of the $\gamma - m$ curve and the known values of mean activity coefficients of sodium chloride solutions. The concentration of amino-acid is so small throughout that its influence on the activity coefficient of the salt may be neglected. The values of Γ_2 in moles/sq. cm. $\times 10^{10}$ calculated in this way are given in Table II. The activity coefficients of sodium chloride solutions were taken from the data of Pease and Nelson³; these were obtained from vapour pressure measurements and are in good agreement with those found by E.M.F. methods. The surface concentrations of water for solutions containing only sodium chloride are also given in the Table; these were calculated from the Gibbs equation applied to a binary system

$$\frac{d\gamma}{dm} = {}_0\Gamma_2 2RT \frac{m}{55.55} \left[\frac{1}{m} + \frac{d \log f_{\pm}}{dm} \right]$$

using surface tension data previously found by the writer.

TABLE II.

Acid. \backslash m_1	0.3	0.5	0.7	0.9	1.25	1.75	2.25	2.75	3.25
Aspartic Acid . .	21.8	19.7	19.2	18.8	17.8	16.6	13.0	12.7	11.6
Asparagine . .	21.2	19.2	18.7	18.3	17.4	16.2	12.7	12.4	11.3
Glutamic Acid . .	20.3	18.4	17.9	17.5	16.6	16.3	12.1	11.9	10.8
o-Amino Benzoic Acid	16.4	15.2	14.8	14.2	13.4	12.6	9.8	9.6	8.7
m-Amino Benzoic Acid	16.7	15.5	15.1	14.4	13.7	12.8	10.0	9.8	8.9
p-Amino Benzoic Acid	19.0	17.6	17.1	16.4	15.5	14.5	11.3	11.1	10.1
—	23.0	20.8	20.3	19.8	18.8	17.4	13.7	12.8	12.0

It appears that the surface concentrations of water are in all cases reduced by the presence of amino-acid. The figures given refer to constant activity of the amino-acid, but not to the same concentration for each. Aspartic acid has a lower solubility than either asparagine or glutamic acid; that of glutamic acid is less than that of asparagine. In the case of the benzoic acids, the solubility of the meta-acid is greatest, that of the ortho-acid being comparable with that of the para. These differences are, however, not great, and probably do not effect the values of $(\partial\gamma/\partial m_1)_{\mu_3}$.

These results may be regarded from the standpoint of the existence of zwitterions in the solutions, and the conclusions compared with those based on titration experiments in the presence of formaldehyde. Glycine produces a larger positive effect on the surface tension than any of the acids quoted above; the value for $(\partial\gamma/\partial m_1)_{\mu_3}$ is 1.7, which is identical with that found for sodium chloride alone. Titration of para-amino-benzoic acid in presence of formaldehyde appears to indicate that the acid is present in the unionised form, while in the case of aspartic acid one of the carboxyl groups is probably unionised. This order is the same as that found for $(\partial\gamma/\partial m_1)_{\mu_3}$ (and also for Γ_2); it appears probable, therefore, that the other benzoic acids are unionised, while asparagine is in a condition similar to aspartic acid. Reliance cannot be placed on small differences, however, as individual effects may have to be taken into account.

³ Pease and Nelson, *J. Amer. Chem. Soc.*, 1932, 54, 3544.

The surface adsorption of amino-acid, which may be either positive or negative, may be calculated from

$$\Gamma_3 = \frac{1}{RT} \left(\frac{\partial \gamma}{\partial m_1} \right)_{\mu_3} / \left(\frac{\partial \log f_3}{\partial m_1} \right)_{\mu_3}$$

an equation previously deduced by the writer (1). Thus if $(\partial \log f_3 / \partial m_1)_{\mu_3}$ is constant, Γ_3 will be independent of salt concentration; the salting out of amino-acids, however, does not always follow a simple relationship.

Summary.

The surface tensions of ternary solutions containing sodium chloride at concentrations from 0.4 molar and saturated with respect to the following amino-acids—*aspartic acid, asparagine, glutamic acid, o-, m-, and p-amino-benzoic acids*—have been measured by the bubble pressure method. The acids produce very little effect on the surface tension of water, but a more marked effect as the concentration of salt increases. The surface tension-salt concentration curve is in all cases a straight line of slope less than that for pure salt solutions. It is shown that under the experimental conditions the activities of the undissociated acid and the ions derived from it are approximately constant, which allows the surface concentrations of water to be calculated by means of the Gibbs equation. In all cases it is found that the presence of amino-acid reduces the amount of water adsorbed. The results are discussed from the standpoint of the zwitterion theory.

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THE EXCHANGE OF HYDROGEN WITH DEUTERIUM IN SOLUTION.

By A. E. BRODSKII.

Received 22nd March, 1937.

If various compounds containing hydrogen are dissolved in heavy water, a mutual interchange of the two isotopes of hydrogen takes place. The final state can be characterised by means of the exchange factor:

$$\alpha = \left(\frac{D}{H} \right) \text{ in water } \div \left(\frac{D}{H} \right) \text{ in solute.} \quad (1)$$

The value of α has been determined for ten substances, representing various chemical types (acids, bases, amines, phenols, etc.),¹ the resulting average figures of which are given in Table I.

The residues from the production of concentrated heavy water at our plant were taken for the exchange. After the exchange was complete, the water was partially distilled off, then carefully purified and analysed

¹ A. E. Brodskii and O. Ch. Scarre, *Acta Physicochim. U.S.S.R.*, 1935, **2**, 603; J. M. Shershever, A. E. Brodskii and M. M. Sluckaia, *ibid.*, 1935, **2**, 611; M. M. Sluckaia, J. M. Shershever and A. E. Brodskii, *ibid.*, in the press; A. E. Brodskii and M. M. Sluckaia, *ibid.*, in the press.

interferometrically.² The separation was made under different pressures. Other details have already been described.¹ For acetone another method (described below) was used. The deviations of the individual experiments from the average values are given in Table I. The slight change of α with the deuterium content of the water (see below) and with the temperature differences during the reaction and the separation of water from the mixtures was neglected in the calculation of the average α , as it does not exceed the experimental errors.

As shown in the Table, in all cases, except acetone, the deviations of α from unity are not greater than the actual experimental errors. The average value is 1.00 for the direct exchange and 0.9, for the less precisely determined reverse exchange. Comparison of published data³ confirms this conclusion: except for the few exceptions mentioned below, α does not greatly differ from unity. For twenty-two substances, investigated by seven authors, the average is 1.04.

TABLE I.—THE EXCHANGE FACTOR FOR VARIOUS DISSOLVED SUBSTANCES.

(h = number of exchangeable hydrogens, n = number of experiments,
 α = for direct exchange, α' = for reverse exchange.)

Substance.		h .	Direct Exchange.		Reverse Exchange.	
			n .	α .	n .	α' .
Sulphuric acid	H ₂ SO ₄	2	3	1.01 \pm 0.03	2	0.94 \pm 0.14
Succinic acid	(CH ₂ · COOH) ₂	2	5	0.98 \pm 0.09		
Glyccol	CH ₂ · NH ₂ · COOH	3	5	0.99 \pm 0.04	4	0.99 \pm 0.04
<i>o</i> -Amino benzoic acid	C ₆ H ₄ · NH ₂ · COOH	3	2	1.01 \pm 0.02		
Hydrazine sulphate	(NH ₂) ₂ · H ₂ SO ₄	6	4	1.04 \pm 0.03	2	0.96 \pm 0.02
Acetamide	CH ₃ · CONH ₂	2	3	1.02 \pm 0.02	1	0.93
Urea	CO(NH ₂) ₂	4	2	0.98 \pm 0.01		
Sodium hydroxide	NaOH	1	3	0.96 \pm 0.04		
Hydroquinone	C ₆ H ₄ (OH) ₂	2	1	(0.9)		
Acetone	CH ₃ · CO · CH ₃	6	3	1.21 \pm 0.01		
Mean (excluding acetone)				1.00 \pm 0.04		0.97

Hydrogen and deuterium are, therefore, found to be distributed between water and the solute in the majority of substances in an almost random manner. This conclusion is certainly valid for most molecules in which the isotopic substitution does not induce any great change in the configuration and in the molecular constants.

The relation between the equilibrium constant for the exchange reaction and the exchange factor α ⁴ can be immediately found only for

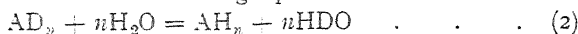
² N. S. Filippova and M. M. Sluckaia, *Acta Physicochim. U.S.S.R.*, 1936, 5, 131, determined the constants necessary for this analysis. The data agree well with those formerly obtained by D. B. Luten, *Physic. Rev.*, 1934, 45, 161.

³ K. W. F. Bonhoeffer and G. W. Brown, *Z. physikal. Chem.*, B, 1933, 23, 171; R. Klar, *ibid.*, 1934, 26, 335; F. K. Münzberg, *ibid.*, 1935, 31, 18; 1936, 33, 23, 39; J. Horiuti and M. Polanyi, *Nature*, 1934, 134, 377; M. Harada and T. Titani, *Bull. Chem. Soc. Japan*, 1936, 11, 465; W. J. C. Orr, *Trans. Faraday Soc.*, 1936, 32, 1033; S. Korman and V. K. Lamer, *J. Amer. Chem. Soc.*, 1936, 58, etc. In some cases the values of α were calculated from the data mentioned in these papers. The figures for α are given in, A. E. Brodskii, *J. physical. Chem. U.S.S.R.*, in the press.

⁴ In spite of the possible variation of α for the different reactions, it is, however, at least provisionally, justifiable to take the general average value from those data where the deviations from unity do not exceed the experimental errors.

those substances which contain a single exchangeable hydrogen atom. For other substances it is necessary to know the distribution of both isotopes between the various kinds of isotopic molecules (AH_n , $AH_{n-1}D$, . . . AHD_{n-1} , AD_n) of the dissolved substance.

In the solution there are the following equilibria



and also $n - 1$ equilibria of the type: $AH_{n-1}D + H_2O = AH_n + HDO$. For the first two equilibria we have:

$$K = \frac{[AH_n][HDO]^n}{[AD_n][H_2O]^n} \quad \text{and} \quad K_0 = \frac{[HDO]^2}{[H_2O][D_2O]} \quad (4)$$

It follows from (1) that

$$\alpha = \frac{x}{1-x} \cdot \frac{\sum_0^{n-1} (n-i) [AH_{n-i}D_i]}{\sum_1^n i [AH_{n-i}D_i]} = \frac{x}{1-x} \cdot \frac{\sum_0^{n-1} (n-1) [AH_{n-i}D_i]}{\sum_0^{n-1} (i+1) [AH_{n-i-1}D_{i+1}]} \quad (5)$$

where x is the atomic fraction of deuterium in water after equilibrium is reached.

If we admit the random distribution of the atoms H and D between various isotopic molecules of the dissolved substances, we can take the concentrations of these molecules as proportional to the expressions:

$$(1-y)^{n-i} y^i \frac{n!}{i!(n-i)!} \quad (6)$$

where y is the atomic fraction of deuterium in the dissolved substance after the equilibrium is reached.

It follows from (6) that:

$$\frac{[AH_{n-i}D_i]}{[AH_{n-i-1}D_{i+1}]} = \frac{(1-y)^{n-i} y^{i+1} (i+1)! (n-i-1)!}{(1-y)^{n-i-1} y^{i+1} i! (n-i)!} = \frac{1-y}{y} \frac{i+1}{n-i}$$

and:

$$\frac{[AH_n]}{[AD_n]} = \left(\frac{1-y}{y} \right)^n$$

Substituting in (5):

$$\alpha = \frac{x}{1-x} \cdot \frac{1-y}{y} = \frac{x}{1-x} \cdot \frac{[AH_n]^{1/n}}{[AD_n]^{1/n}}$$

and with (4):

$$\alpha = \frac{1}{2} \psi(x) \cdot k^{1/n} \quad (7)$$

where:

$$\psi(x) = 2 \frac{x}{1-x} \frac{[H_2O]}{[HDO]} \quad (8)$$

The distribution (6) should not, in the majority of molecules mentioned above, differ significantly from the actual distribution, since the replacement of H by D does not greatly alter the configuration of the molecules and the difference of the zero-point energies, but influences principally only the symmetry numbers.⁵

If the distribution of the hydrogen isotopes in the molecules H_2O , HDO and D_2O also takes place in a random manner, we have $\psi(x) = 1$

⁵ See also, H. C. Urey and L. Greiff, *J. Amer. Chem. Soc.*, 1935, **57**, 321; W. F. Giauque and R. Overstreet, *ibid.*, 1932, **54**, 1731.

and $\alpha = k^{1/n} = \text{const}$. In reality, the value of k_0 differs considerably from the statistical value 4. At 25° , $k = 3.26$ and therefore $\psi(x)$ rises almost linearly⁷ from 1 at $x = 0$ to 1.227 at $x = 1$. This causes a change in α of about 1/5 when x increases from 0 to the limiting value 1 (taking k as constant).⁸ When $n = 1$, the expression (7) is valid independent of the assumption (6).

For most exchange reactions of complicated molecules in solution, α tends to unity, when x is small; therefore k may also be expected not to differ greatly from this value.⁹

The really significant deviations of α from unity are found for acetone. The results of different investigators differ considerably.¹⁰ Therefore with M. Sluckaia I have repeated the measurements by a more precise method, which is a modification of that recently suggested by W. J. C. Orr³ for the exchange in ethyl alcohol. An excess of carefully dehydrated borax was added to the solution after the equilibrium was reached. Then, the hydrated borax was separated from the solution by sucking off and wringing out on a filter paper, and dried at 60° . Finally the water of crystallisation was distilled out by heating up to 250° and analysed in the usual way. Check experiments proved the absence of fractionation of the isotopes and of the absorption or combination of acetone by borax. The dried acetone contains traces of alkali sufficient to secure the enolisation. The experiments were made at 18° to 20° . The results are represented in Table II.,

TABLE II.—THE EXCHANGE IN ACETONE AT 18° – 20° .

g.	g ₀ .	G.	τ .	x_0 .	x .	α .
10.4192	11.9438	10	24	1.92	1.14	1.20
22.7282	29.6102	11	24	1.19	0.75	1.22
—	—	9	48	—	0.75	1.22

⁶ B. Topley and H. Eyring, *J. Chem. Physics*, 1934, 2, 217; the value of $\psi(x)$ does not vary greatly with temperature.

⁷ From (a) $[\text{HDO}]^2 = K_0[\text{H}_2\text{O}] \cdot [\text{D}_2\text{O}]$; (b) $[\text{HDO}] + 2[\text{D}_2\text{O}] = x$; (c) $[\text{HDO}] + 2[\text{H}_2\text{O}] = 1 - x$ and (8)

we have:
$$\frac{[\text{H}_2\text{O}]^2}{[\text{HDO}]^2} = \frac{1-x}{K_0x} - \frac{2x-1}{2x} \frac{[\text{H}_2\text{O}]}{[\text{HDO}]}$$

or:
$$\psi^2 + \frac{2x-1}{1-x} \psi - \frac{4x}{K_0(1-x)} = 0$$

from which ψ can be calculated for various values of x , if $K_0 = 3.26$.

⁸ In our measurements, where x changed only from 0.5 to 4.6 per cent., the variation of α with x is less than 1 per cent., *i.e.*, less than the experimental errors.

⁹ When x is small, so that we can neglect the content of D_2O , $\text{AH}_{n-2}\text{D}_2 \dots \text{AD}_n$ molecules, it follows from (5), in agreement with the relation obtained by Harada and Titani³:

$$\alpha = \frac{x}{1-x} \cdot \frac{n[\text{AH}_n]}{[\text{AH}_{n-1}\text{D}]} = \frac{n}{2} \psi(x) \cdot k' \simeq \frac{n}{2} k'$$

for the reaction $\text{AH}_{n-1}\text{D} + \text{H}_2\text{O} = \text{AH}_n + \text{HDO}$ with the equilibrium constant:

$$k' = \frac{[\text{AH}_n][\text{HDO}]}{[\text{AH}_{n-1}\text{D}][\text{H}_2\text{O}]}$$

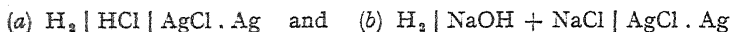
¹⁰ K. Schwarz and H. Steiner, *Z. physikal. Chem.*, B, 1934, 25, 153 ($\alpha = 1.3$ at $x = 8$ per cent.); R. Klar² ($\alpha = 1.1$ to 1.4 at $x = 0.5$ to 10.2 per cent.); J. O. Halford, L. C. Anderson, J. R. Bates and R. D. Swisher, *J. Amer. Chem. Soc.*, 1934, 56, 491; 1935, 57, 1663 ($\alpha = 1.17$ to 1.35 at $x = 2.4$ to 12.0 per cent. in the final measurements). The last authors found respectively $k_1 = 2.1$ and $k_2 = 4$ for the reactions: $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2\text{D} + \text{H}_2\text{O} = \text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 + \text{HDO}$ and $\text{CH}_3 \cdot \text{CO} \cdot \text{CHD}_2 + 2\text{H}_2\text{O} = \text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 + 2\text{HDO}$, or $k_1^2/k_2 = 1.1$ instead of $k_1^2/k_2 = 12/5$ calculated from a simplified function for the entropy, in complete agreement with the value following from (6).

where g represents gm. acetone; g_0 , gm. water; G , gm. borax; τ , time of exchange in hours and x and x_0 , the initial and final atomic fraction of deuterium in water.

The considerable deviation of α from unity for this reaction can probably be ascribed to the keto-enol tautomerism, which must considerably alter the distribution (6) from a random one. The measurements of Münzberg³ give further proof of this assumption. He has investigated the velocity of the exchange in some di- and trioxybenzenes and has found $\alpha = 1$ for the exchange in the hydroxyl hydrogens and $\alpha = 1.15$ for the slower exchange of the nuclear hydrogens, accompanied by enolisation. The latter value is in accordance with our value, found for acetone.¹¹ The comparatively small value for some carbohydrates found by Hamill and Freudenberg,¹² may be ascribed to similar causes.

Our value of α for the exchange in succinic acid was confirmed by Münzberg ($\alpha = 0.95$).

The value 1.02 found by Korman and La Mer¹³ for hydroquinone is also in agreement with our measurements. However, taking into account this value, their own precise measurements of quinhydrone cells in D_2O and the measurements of Abel, Bratu and Redlich¹⁴ of the acid and alkali cells, they calculated¹⁵ $K = \sqrt{2.42} = 1.56$ for the reaction: $2NaOD + H_2O = 2NaOH + D_2O$, which differs from our $K = 1.05 \pm 0.05$. The different temperature (about 100° in our case) cannot explain this discrepancy, which probably arises from the data of Abel, Bratu and Redlich. These authors determined the values: $\Delta E_H = E'_b - E'_a$ and $\Delta E''_D = E''_b - E''_a$ in H_2O and D_2O for the cells:



i.e., involving small differences of large numbers, extrapolated to $x \rightarrow 1$. By replacing their value¹⁶ of $\Delta E_D - \Delta E_H = 0.0465 v$ by $0.036 v$ we obtain the right value for K . The discrepancy may also, in some measure, be ascribed to the doubtful¹⁷ assumption, in the calculation of ΔE , of equal solubility of $AgCl$ in H_2O and in D_2O .

An interesting example of a large disturbance in the random distribution is the exchange in HCl , for which, Korman and La Mer¹³

found $K = \frac{[HCl][D_2O]^{\frac{1}{2}}}{[DCl][H_2O]^{\frac{1}{2}}} = \sqrt{15.30} = 3.9$. The reason of this abnormal behaviour is clear when the spectroscopic data are considered.¹⁸

Harada and Titani³ have made an interesting attempt to correlate the values of α and the strengths of acids or bases in the light of Brönsted's well-known theory; comparison of Table I. and other published data do not, however, confirm the general validity of this relation.

¹¹ After writing this paper, I learnt of a recent paper of K. Wirtz, *Z. physik. Chem., B*, 1935, 34, 121, which discusses a similar problem. For the exchange in acetone, he calculated from spectroscopic data $\alpha = 1.088$ at 80° . It follows that $\alpha = 1.092$ at 25° instead of my figure of 1.082 . Taking into account the approximations used in the calculation, the concordance is good.

¹² W. H. Hamill and W. Freudenberg, *J. Amer. Chem. Soc.*, 1935, 57, 1427.

¹³ S. Korman and V. K. La Mer, *J. Amer. Chem. Soc.*, 1936, 58, 1396.

¹⁴ E. Abel, E. Bratu and O. Redlich, *Z. physikal. Chem., A*, 1935, 173, 353.

¹⁵

$$K = \frac{[NaOH][D_2O]^{\frac{1}{2}}}{[NaOD][H_2O]^{\frac{1}{2}}}$$

¹⁶ The measurements of B. Topley and W. F. K. Wynne-Jones, *Nature*, 1934, 134, 574, give $0.028v$.

¹⁷ Having regard to the behaviour of other salts, see also C. Drucker, *Trans. Faraday Soc.*, 1937, 33, 660.

¹⁸ Thermodynamic calculation from the spectroscopic data gives for gaseous HCl : $K = 2.6$ to 2.8 at $298.1^\circ K$. See H. C. Urey and D. Rittenberg, *J. Chem. Physics*, 1933, 1, 137; B. Topley and H. Eyring⁶; A. Farkas, *Heavy Hydrogen*, 1935, p. 180; see also the recent calculations of K. Wirtz.¹¹

Summary.

(1) The exchange of hydrogen with deuterium in solution has been investigated for ten different substances. In all cases, except acetone, the exchange factor α is approximately unity. Examination of published data confirms this value for most exchange reactions with complicated molecules.

(2) The relation between α and the equilibrium constant of the exchange reaction has been established by an assumption as to the distribution of H and D atoms between the isotopic molecules. It is shown that α is not constant for various D-contents in the solution.

(3) The value of α for acetone is 1.21 ± 0.01 at 18° to 20° ; the considerable deviation of this value from unity is ascribed to tautomeric transformation.

(4) Some other exchange reactions are discussed.

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THE RATE OF UNIMOLECULAR AND BIMOLECULAR REACTIONS IN SOLUTION AS DEDUCED FROM A KINETIC THEORY OF LIQUIDS.

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List of Symbols Used.

a	Mean displacement of the centre of a molecule between the extremes of oscillation.
α	Probability of return after a collision.
A_1, A_2	Constants in the formula for k (equation 28).
b	Coefficient in the formula for ν ($\nu = \nu_0 + bT$).
β	Compressibility.
B	Constant in the formula for k (equation 28).
c	Constant given by $ac = \frac{1}{2}mv^2$.
d	Displacement of a molecule during diffusion.
d_{12}	Sum of the radii of molecules 1 and 2.
d_1	Sum of the radii of molecule 1 and the solvent molecule.
D	Diffusion coefficients.
E	Activation energy of reaction.
E_2	Activation energy of diffusion.
E_3	Observed activation energy given by $k = ze^{-E_2/RT}$ or $D = \text{const. } e^{-E_3/RT}$.
f	Half the number of squared terms defining the activation energy.
γ	Fraction of collisions effective for reaction.
h	Velocity coefficient.
k	Gas constant per molecule.
L	Molecular latent heat of evaporation.
m	Mass of a molecule.
M	Molecular weight of a molecule.
n	Number of molecules per c.c.
N	Avogadro's number.
ν	Vibration frequency (complete oscillations).
p	Pressure.
$[P]$	Parachor.
r	Radius of a molecule.
r_s	Radius of a solvent molecule.
r_0	Value of r extrapolated to the absolute zero.

R	Gas constant per gm. molecule.
ρ	Density.
t	Time.
T	Absolute temperature.
τ	Period of half a complete oscillation of a molecule.
v	Velocity of a molecule.
V	Molecular volume.
V_0	Value obtained by extrapolating V for a liquid to the absolute zero.
z	Collision frequency.
η	Viscosity.

In this paper, which is an extension of a previous paper of the author,¹ an attempt is made to derive collision frequencies and reaction rates in solution from the theory of the liquid state. The energy of activation E will be treated as an experimentally derived magnitude which enables the collision frequency z to be calculated, and hence agreement between theoretical and observed values of z cannot be expected to be very exact, since the observed values of z will be sensitive to small changes in E .

I. A Kinetic Theory of Liquids.

The starting point of this paper is the conception of a liquid as a system of oscillators, which was developed by the author¹ and independently by T. S. Wheeler, who in subsequent papers has considered the whole range of liquid phenomena, as well as reaction velocity.²

There is considerable evidence in favour of the view that a liquid, if not too far removed from its melting-point, resembles the solid rather than the gaseous state of matter, and that many liquids possess a quasi-crystalline structure. Reference may be made to the work of Bernal and Fowler on water³ the X-ray diffraction patterns of liquids,⁴ the phenomenon of "wings" in the Raman spectra of liquids (see later), etc. Each molecule of a liquid may be supposed to be rushing to and fro in an approximately spherical space or "cage" bounded by adjacent molecules, so that the motion may be reduced to an oscillation with continually changing axes. Owing to the rotation of molecules the assumption of spherical cages is much nearer the truth than would at first sight be suspected.

This representation of the liquid state suggests that only when a molecule has sufficient energy to break through the cage does self-diffusion occur. Andrade has expressed similar views with regard to viscosity.⁵

The Frequency of Oscillation.

The virtual radius r , i.e., the radius of the spherical space in which a molecule executes thermal motion, is given by $r = \left(\frac{3 \times 0.74M}{4N\rho} \right)^{\frac{1}{3}}$. The period of half a complete oscillation, τ , is given by

$$\tau = \frac{a}{v} = a \left(\frac{m}{3kT} \right)^{\frac{1}{2}} \quad \dots \quad (I)$$

since $\frac{1}{2}mv^2 = \frac{3}{2}kT$.

¹ J.C.S., 1934, 1910.

² (a) *Indian J. Physics*, 1934, 8, 521; (b) *Proc. Indian Acad. Sci.*, 1934, 1, 105; (c) *ibid.*, 1935, 1, 795; (d) *ibid.*, 1935, 2, 1; (e) *ibid.*, 1935, 2, 466; (f) *ibid.*, 1936, 4, 291; (g) *ibid.*, 1936, 4, 298.

³ *J. Chem. Physics*, 1933, 1, 515.

⁴ Cf. Stewart, *Rev. Modern Physics*, 1930, 2, 116.

⁵ *Phil. Mag.*, 1934, 17, 501, 750; cf. also Eyring, *J. Chem. Physics*, 1936, 4, 283.

This simple equation may be improved by the consideration that as a general rule the density of a liquid varies linearly with temperature, and hence

$$\begin{aligned} r &= r_0 + bT \text{ where } b \text{ is a constant,} \\ a &= 2(r - r_0) = 2bT \end{aligned} \quad (2)$$

Hence a is proportional to the temperature and to the mean kinetic energy, so that

$$ac = \frac{1}{2}mv^2, \text{ where } c \text{ is a constant.}$$

The number of molecules per c.c. with kinetic energy between E/\mathbf{N} and $\frac{E + dE}{\mathbf{N}}$ is dn which is proportional to $ne^{-E/RT}dE$, where n is the number of molecules per c.c., and these will have periods between τ' and $\tau' + d\tau'$, where $\tau' = a'/v' = \frac{1}{2}mv'/c = \left(\frac{Em}{2\mathbf{N}}\right)^{\frac{1}{2}} \frac{1}{c}$. Hence the mean half-period is given by

$$\tau = \frac{\int_0^\infty \left(\frac{Em}{2\mathbf{N}}\right)^{\frac{1}{2}} \frac{1}{c} e^{-E/RT} dE}{\int_0^\infty e^{-E/RT} dE} = \frac{v\pi \left(\frac{RTm}{\mathbf{N}}\right)^{\frac{1}{2}} \frac{1}{c}}{2} = \frac{a}{v} \left(\frac{\pi}{3}\right)^{\frac{1}{2}} \quad (3)$$

The summation is conducted in a slightly different manner from that used in the previous paper, and hence results differ by a small numerical factor. The value $\tau = \frac{a}{v} \left(\frac{\pi}{3}\right)^{\frac{1}{2}}$ will be used instead of $\tau = a/v$.

The frequency ν of a complete oscillation is given by

$$\nu = \frac{1}{2\tau} = \frac{3}{2a} \left(\frac{kT}{\pi m}\right)^{\frac{1}{2}} \quad (4)$$

Since $a = 2(r - r_0) = 2\left(\frac{3}{4\pi} \times \frac{0.74}{\mathbf{N}}\right)^{\frac{1}{2}} (V^{\frac{1}{2}} - V_0^{\frac{1}{2}})$ where V and V_0 are the molecular volumes at T and at the absolute zero, the latter value being obtained by extrapolation from values in the liquid state, it follows that

$$\nu = \frac{5.8 \times 10^{11} \cdot T^{\frac{1}{2}}}{M^{\frac{1}{2}}(V^{\frac{1}{2}} - V_0^{\frac{1}{2}})} \quad (5)$$

Wheeler has shown ^(e) that if we assume a law of force between liquid molecules which varies with the inverse m th power of the distance, and if we assume that $m = 11$,

$$\nu = \frac{16}{7} \left(\frac{6}{\pi}\right)^{\frac{1}{2}} \left(\frac{[P]}{V}\right)^{\frac{4}{5}} \frac{r}{(mkT)^{\frac{1}{5}}} \quad (6)$$

Values deduced by equations (5) and (6) are in substantial agreement.

The Raman Spectra of Liquids and the Phenomenon of "Wings"; Other Evidence in Support of the Theory.

If there are really vibrations in liquids of the type discussed above, their presence should be revealed by Raman spectra. It has long been known that a continuous spectrum occurs near the exciting line and extends on both sides of it to 15-20 Å, the so-called phenomenon of "wings." These low vibrations were at first attributed to rotational motion.

Bhagavantam and Rao⁶ find, however, that for benzene the intensity distribution is quite different from the requirements of a rotational spectrum. Gross and Vuks⁷ have studied lines associated with lattice vibrations. If we calculate the frequency of the liquids studied by Gross and Vuks at the melting-point we obtain remarkably good agreement with the mean Raman frequency observed in the spectra of the solids, as is seen in Table I.

TABLE I.

Compound.	Raman Frequency Shifts near Exciting Line, cm.^{-1} .	Mean Raman Frequency.	ν at m.p. from Equation 5.	(in \AA.U.).
C_6H_6	62, 104	2.49×10^{12}	2.44×10^{12}	0.560
$p\text{-C}_6\text{H}_4\text{Br}_2$	20, 38, 93	1.50×10^{12}	2.07×10^{12}	0.578
C_{10}H_8	45, 73, 109, 124	2.64×10^{12}	2.69×10^{12}	0.473

The Diffusion Coefficient.

According to the theory above a solute molecule can escape from its cage only when endowed with sufficient energy, E_2 per gm. molecule, to force its way through the barrier. Diffusion will proceed by a series of jumps, each equal to d . Consider a tube of unit cross section and select two planes, 1 and 2, of distance d apart, at which the concentrations are n_1 and n_2 . The number of solute molecules at plane 1 may be taken as dn , the solute being confined within a region of thickness d . Hence if we divide the molecules into six groups, the number of molecules leaving plane 1 along the axis of the tube towards plane 2 is $\frac{E_2}{RT} \frac{dn_1}{6} e^{-E_2/RT}$ in time τ and similarly for plane 2. The factor E_2/RT allows for the $2f$ degrees of freedom of the colliding molecules, *i.e.*, $2f = 4$, for the energy of each molecule (solute and solvent at the wall), can be expressed by 2 squared terms, oscillation potential and kinetic energy.

It follows that the net flow per sec. per sq. cm. is given by

$$\frac{d}{12\tau}(n_1 - n_2) \frac{E_2}{RT} e^{-E_2/RT} = \frac{D}{d}(n_1 - n_2) \text{ where } D \text{ is the diffusion coefficient.}$$

$$\text{Hence } D = \frac{d^2}{12\tau} \frac{E_2}{RT} e^{-E_2/RT} = \frac{d^2}{4a} \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \frac{E_2}{RT} e^{-E_2/RT} \quad (7)$$

Unlike the usual deduction which employs Stoke's Law, *viz.*, $D = \frac{RT}{3\pi\eta N r}$, equation (7) does not involve η explicitly (and η for a molecule can have little meaning) and the temperature coefficient resembles that for a chemical reaction.

The plot of $\log D$ against $1/T$ does indeed give a straight line. d is given by $r_1 + r_s$, where r_1 and r_s are the virtual radii of solute and solvent molecules. The results are summarised in Table II. and it will be seen that good agreement is obtained.

Wheeler^{2(s)} has incorporated his formula for ν (equation (6)) into equation (7). He considers that the internal energy of the molecules can become operative, the critical energy E_2 being defined by $2f$ squared terms.

Low values of f are required to give agreement with experiment.

⁶ *J. Indian Physics*, 1934, 8, 437.

⁷ *Nat.*, 1935, 135, 100, 431, 998.

TABLE II.

Solute.	Solvent.	$E_3 = E_2 - \frac{3}{2}RT.$	$D_{obs. 25^\circ C.}$	$D_{calc. 25^\circ C.}$ (eqn. 7).
PhOH	MeOH	3151	1.79×10^{-5}	1.15×10^{-5}
PhOH	C_6H_6	3078	1.84×10^{-5}	1.21×10^{-5}
Sym- $C_2H_2Br_4$	Sym- $C_2H_2Cl_4$	3365	0.61×10^{-5}	0.72×10^{-5}
Br_2	CS_2	1536	3.32×10^{-5}	3.41×10^{-5}
$CaCl_2$	H_2O	4410		
KCl	H_2O	3960		

II. "Unimolecular" Reactions in Solution.

In the treatment of the rate of a reaction in solution by a collision process very little attempt has been made to relate the problem to the molecular theory of liquids.⁸ Previous workers have given the number of collisions between solute and solvent molecules, which determines the rate of a unimolecular reaction, the value $6\pi\eta r/2m$, where m is the mass of the solute molecule. Few would deny, however, that Stoke's law even in its refined form due to Cunningham, Millikan and Epstein⁹ cannot be applied to a molecule. The treatment in this paper is essentially different, and diffusion enters into the consideration of bimolecular but not of unimolecular reactions.

"Unimolecular" Reactions in the Liquid Phase (Pure Liquid).

Equation (4) is directly applicable to the rate of a unimolecular reaction in a pure liquid. The process is essentially bimolecular, and each molecule in the collision complex contributes two squared terms, kinetic and oscillation potential, to the activation energy, making four squared terms in all. This introduction of squared terms differs from that of Moelwyn-Hughes in that it is the same for all reactions and does not include *internal* degrees of freedom. The allocation of internal degrees of freedom is uncertain, and their introduction removes the possibility of testing the formula by experiment.

From equation (4) it follows that the number of collisions which each molecule makes with the surrounding walls is $2\nu = 1/\tau$ per sec., since a collision occurs at each resting point of the libration, and if there are n molecules per cubic centimetre the total number of collisions per cubic centimetre per sec.

$$= \frac{1}{2} n \cdot 2v \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

since in summing over one cubic centimetre each molecule is counted twice. If all collisions between a molecule and its envelope in which the energy exceeds the critical increment E are effective for reaction, the velocity coefficient is given by

$$k = \frac{1}{2} \cdot 2\nu \cdot \left(\frac{E}{RT} \right) e^{-E/RT}$$

$$= \frac{3}{2a} \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \frac{E}{RT} e^{-E/RT} \quad (9)$$

⁸ Cf. Christiansen, *Z. physik. Chem.*, 1924, 113, 35; Jowett, *Phil. Mag.*, 1929, 8, 1059; Moelwyn-Hughes, *The Kinetics of Reactions in Solution*.

⁹ Cf. *Physic. Rev.*, 1924, 23, 710.

The factor E/RT allows for four squared terms. Since

$$d \log_e k/dT^{-1} = -E/R + \frac{3}{2}T,$$

a being proportional to T the true value of E is obtained by adding $\frac{3}{2}RT$ to the value given by the slope of the "straight line" on the graph of $\log k$ against $1/T$. If we denote this last value by E_3 , $E = E_3 + \frac{3}{2}RT$ and

$$k = \frac{3}{2a} \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \frac{E}{RT} e^{-3/2} e^{-E_3/RT} = ze^{-E_3/RT} \quad (10)$$

An example is provided by the conversion of *d*-pinene into dipentene. Unfortunately E_3 was not measured for the liquid, but for the gas and for petroleum solution the values 43,710 cal. and 41,210 cal. were obtained.¹⁰ We may use equation (9) to calculate a value of E from the observed velocity coefficient at 457.5° obs., viz., 4.99×10^{-7} ; the value calculated, 41,860 cal., is very near E_3 in the petroleum solution and is thus probably near to the actual value.

"Unimolecular" Reactions in Solution.

For unimolecular reactions in solution the assumption that collisions between solute and solvent molecules of energy greater than E lead to reaction gives

$$k = \frac{3}{a} \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \frac{E}{RT} e^{-E/RT} \quad (11)$$

The factor $\frac{1}{2}$ is not included since in summing over 1 c.c. each molecule is counted only once.

As an example the reaction $\text{CCl}_3 \cdot \text{CO}_2\text{H} \rightarrow \text{CHCl}_3 + \text{CO}_2$ in aniline will be considered. Equation 11 gives $k = 0.68 \times 10^{-7}$ whereas the observed value¹¹ is $6.7 \times 10^{-7} \text{ sec.}^{-1}$. The value calculated using equation (6) for ν and calculating the parachor by the additivity relationship is 1.07×10^{-7} . This is sufficiently good agreement since E_3 is liable to an error of 1000 cal.

The decomposition of diethyl malonic acid in water proceeds $\text{CEt}_2(\text{CO}_2\text{H})_2 \rightarrow \text{CHEt}_2 \cdot \text{CO}_2\text{H} + \text{CO}_2$, and ν may be calculated sufficiently accurately from Beilstein's data for the isomeric diethyl malonate. $E_3 = 33,430$, and k may be calculated from equation (9) to be $0.16 \times 10^{-8} \text{ sec.}^{-1}$, the observed value¹² being $2.0 \times 10^{-8} \text{ sec.}^{-1}$. If equation (6) be used for ν , $k = 0.20 \times 10^{-8}$.

In the majority of cases the density data will be lacking, partly because many of the molecules used are unstable.

A suitable equation is obtained by inserting the value of ν from equation (6) in equation (9), and multiplying by 2. This gives

$$k = 2.8 \times 10^{12} \frac{[P]^4}{M^{\frac{1}{2}}V^{11/8}} \cdot \frac{E}{RT^{3/2}} e^{-E/RT} \quad (12)$$

Values of $[P]$ may be calculated with considerable accuracy from the atomic and constitutive constants. Values of V are most accurately calculated by determining V from ρ for a related compound.

Results are given in Table III., the reaction velocity data being

¹⁰ Cf. Smith, *J. Amer. Chem. Soc.*, 1927, 49, 43; Conant and Carlson, *ibid.*, 1929, 51, 3464.

¹¹ Goldschmidt and Brauer, *Ber.*, 1906, 39, 109.

taken from Moelwyn-Hughes.¹² Some of the values of $[P]$ are taken from Wheeler.

TABLE III.

Compound Decomposing.	Solvent.	$[P]$.	T° abs.	$E_{\text{cals.}}$	$k_{\text{obs.}}$ sec.-1.	$k_{\text{calc.}}$ eqn. (12). sec.-1.
<i>o</i> -toluene diazonium chloride	H ₂ O	353.3	333	23,440	8.97×10^{-3}	7.91×10^{-3}
<i>m</i> -toluene diazonium chloride	H ₂ O	353.3	333	22,800	8.89×10^{-3}	19.7×10^{-3}
Mesoxalic acid	H ₂ O	218.2	333	33,700	1.82×10^{-8}	0.125×10^{-8}
Triethylsulphonium bromide	AcOH	401.5	333	31,060	8.51×10^{-7}	1.67×10^{-7}
Acetone dicarboxylic acid	H ₂ O	296.2	333	23,320	5.48×10^{-2}	0.46×10^{-2}
Benzene diazonium chloride	H ₂ O	314.3	333	23,360	3.43×10^{-3}	10.7×10^{-3}
2 : 4 : 6 trinitrobenzoic acid	H ₂ O	442.8	333	29,970	3.33×10^{-6}	0.24×10^{-6}
Camphor carboxylic acid	PhCOMe	475.3	333	28,960	1.59×10^{-6}	2.25×10^{-6}
" " "	H ₂ O	475.3	333	29,640	3.31×10^{-7}	8.40×10^{-7}

In contrast to the method of Moelwyn-Hughes the collision frequency z is independent of the viscosity, and $\log z$ varies only slightly with temperature. Wheeler^{2(f)} has also considered unimolecular reactions in the light of the author's theory and has incorporated his (Wheeler's) value for ν (equation (6)) into the theory.

III. Bimolecular Reactions in Solution.

The current view of bi-molecular reactions consists in equating the collision frequencies in the gas and in solution, and all question of mechanism is thus waved aside.

In fairly dilute solution, at a given instant most of the solute molecules will be entirely surrounded by solvent molecules, and only for a small fraction will there be adjacent solute molecules, for which bimolecular reaction is immediately possible. Consider now a series of times after the instant chosen. Further reaction must proceed by diffusion, the number of adjacent pairs statistically possible being continuously replenished. With concentrated solutions on high activation energies of reaction diffusion will not be a controlling mechanism. If the number of solute and solvent molecules per cubic centimetre is n_s and n_1 , the probability that any given molecule next to a solute molecule is also solute is $n_1/(n_1 + n_s)$: as reaction proceeds the adjustment to give the probability distribution is not, however, instantaneous. If we assume for the moment that solute and solvent have approximately equal radii, twelve molecules will be adjacent to any given molecule, and of these $n_1/(n_1 + n_s)$ will be solute, so that the condition that on the average more than one solute molecule is adjacent to a given solute molecule is that $12n_1/n_1 + n_s > 1$ or $n_1 > n_s/11$. With solutions in water this would give a solute concentration of approximately $4N$, so that it is only for these concentrated solutions that the diffusion method does not apply. Fortunately, as will be seen later, the two regions obey formulæ which are nearly equivalent, and diffusion formulæ may be applied even when activation energies are high.

For weak solutions we may apply the theory of Smoluchowski.¹³ If n_1 and n_2 are the number of solute molecules per cubic centimetre,

¹² Moelwyn-Hughes, *op. cit.*,⁸ 164.

¹³ *Z. physik. Chem.*, 1918, 92, 129.

and D_1 and D_2 the diffusion coefficients, the number of molecules of species 2 diffusing up in time t to within a distance d of the n_1 molecules of species 1 in 1 c.c., d being measured from centre to centre, is

$$\int_0^t 4\pi(D_1 + D_2)n_1n_2d \left[1 + \frac{d}{\pi Dt} \right] dt = 4\pi d(D_1 + D_2)n_1n_2t + 8\pi^{\frac{1}{2}}(D_1 + D_2)^{\frac{1}{2}}d^2n_1n_2t^{\frac{1}{2}} \quad (13)$$

The argument whereby Smoluchowski derives this expression appears to be somewhat artificial, notably in the use of a concentration gradient, and has been criticised by Harper,¹⁴ who, however, obtains the same result as Smoluchowski by a different method. Fuchs¹⁵ also supports the result by a less ambiguous analysis.

If $t \gg d^2/(D_1 + D_2)$, the second term is negligible in comparison with the first. This has led to some misunderstanding on the part of Moelwyn-Hughes¹⁶ who has criticised this step, which was adopted by Smoluchowski, on the grounds that if t is the time between successive collisions the second term is not negligible. While this is true it should be pointed out that t in equation (13) is actually an integrated time (written as Δt , not dt , in the previous paper) and is made up of a very large number of diffusion jumps. Equation (13) is in fact valid so long as n_1 and n_2 remain approximately constant during the time interval t , so that t really corresponds with the smallest convenient time interval on the graph of n_1 and n_2 against time such that over this interval n_1 and n_2 are to all intents and purposes constant. The relationship $t \gg d^2/(D_1 + D_2)$ is therefore true.

About one in 35 of the solute oscillations (of a molecule 2) are effective for diffusion away from the cage surrounding it at 25° C., assuming an energy of activation for diffusion of 3000 cal., and about one in 12 of the oscillations of a solute molecule 1 are effective for collision with any particular molecule in the cage surrounding it, in this case a molecule of solute 2 which has diffused up to 1. Hence we may assume that every molecule of species 2 which diffuses up to within striking distance of molecule 1 will be hit by the latter before diffusion away occurs. Hence the number of collisions of molecule 2 with molecule 1 in time t is

$$\frac{1}{2} \cdot 4\pi d(D_1 + D_2)n_1n_2t \quad (14)$$

where the factor $\frac{1}{2}$ allows for counting each molecule twice. As a further refinement this result should be multiplied by a small factor > 1 to allow for the recurrence of collisions, but for simplicity this will be omitted for the present (*cf.* the discussion after equation (21)). If the rate is expressed in the form $dn/dt = kn_1n_2 \frac{1000}{N}$, *i.e.*, using gm. mols. per litre, then

$$k = 2\pi d_{12}(D_1' + D_2') \frac{N}{1000} \frac{E}{RT} e^{-(E+E_2)/RT},$$

where $(D_1 + D_2) = (D_1' + D_2')e^{-E_2/RT}$, and E_2 is the activation energy for diffusion, taken to be the same for each species for simplicity. If we insert the values of D_1 from equation (7) we obtain

$$k = 2\pi \frac{d_{12}}{6} \frac{N}{1000} (d_1^{2\nu_1} + d_2^{2\nu_2}) \frac{E_2}{RT} \cdot \frac{E}{RT} e^{-(E+E_2)/RT} \quad (15)$$

¹⁴ *Trans. Faraday Soc.*, 1936, **32**, 1139.

¹⁵ *Acta Physico chim.*, 1936, **4**, 173, *cf.*, p. 182.

¹⁶ *Ibid.*, 1146.

where $d_1 = r_1 + r_s$, $d_2 = r_2 + r_s$ and $d_{12} = r_1 + r_2$. As before, the energy of activation obtained from the temperature coefficient of k , $E_3(k = ze^{-E_3/RT})$ is related to the true value $E + E_2$ by the equation

$$E_3 = E + E_2 - \frac{5}{2}RT, \text{ or } E = E_3 - E_2 + \frac{5}{2}RT.$$

Very little error will be introduced by assuming that $E_2 = 3000$ cal., since $E_2 + E$ is fixed by experiment, whatever value be assigned to E_2 , and the choice of a value will therefore affect only the factors $\frac{E_2}{RT}$ and $\frac{E}{RT}$ and not the exponential factor. The choice of the equation for ν depends on the experimental data available, and equation (6) is probably the most convenient.

This gives

$$k = 8.88 \times 10^{32} d_{12} \left(\frac{d_1^2 [P_1]^4}{V_1^{11/3} M_1^{1/2}} + \frac{d_2^2 [P_2]^4}{V_2^{11/3} M_2^{1/2}} \right) \frac{E_2 E}{R^2 T^{5/2}} e^{-(E+E_2)/RT} \quad (16)$$

and

$$z = 8.88 \times 10^{32} d_{12} \left(\frac{d_1^2 [P_1]^4}{V_1^{11/3} M_1^{1/2}} + \frac{d_2^2 [P_2]^4}{V_2^{11/3} M_2^{1/2}} \right) \frac{E_2 E}{R^2 T^{5/2}} e^{-5/2}. \quad (17)$$

A result similar to equation (14) was obtained by Ölander, using however an argument which involved viscosity.¹⁷ Ölander gave for z the value

$$z = \frac{\pi}{6} \frac{kT}{\eta} \frac{(r_1 + r_2)^2}{r_1 r_2} \quad (18)$$

If we eliminate η by the equations $D_1 = kT/6\pi\eta r_1$, $D_2 = kT/6\pi\eta r_2$ which were used by Ölander (although their significance is doubtful) we obtain $z = \pi^2(D_1 + D_2)(r_1 + r_2)$, which is similar to equation (14). But equations (18) and (17) are not really equivalent, since equation (17) avoids the doubtful introduction of viscosity.

Suitable examples of unionised bimolecular reactions are rare. There are, however, at least three reactions which have been studied in the gaseous phase and in solution, and for which the velocity coefficient and activation energy are stated to be the same in both phases. Hence k_s/k_g , the ratio of the coefficients in the solution and gas, should be approximately unity, where

$$k_s/k_g = 2.8 \times 10^{12} \pi \left[\frac{d_1^2 [P]^4}{V_1^{11/3} M_1^{1/2}} + \frac{d_2^2 [P]^4}{V_2^{11/3} M_2^{1/2}} \right] \frac{E_2 E}{R^2 T^{5/2}} \bigg/ d_{12} [8\pi RT (M_1^{-1} + M_2^{-1})]^{1/2} \quad (19)$$

Since $E_3 = E + E_2 - 5/2 RT$ for the solution we may still have $E_3 =$ approximately E , even although there is an energy of activation for diffusion. In the first reaction considered below the energy of activation is zero and the E/RT factor is omitted. Results are given in Table IV.

Using the "Ölander-Bradley method" Moelwyn-Hughes obtains a value $k_s/k_g = 1800$ for (a), 1050 for (b) and 1500 for (c).

Agreement is good for reaction (a), where it should be noticed, E_3 is probably truly zero. But in reactions (b) and (c) it is doubtful whether equality of activation energies is secured in the gaseous phase and in

TABLE IV.¹⁸

Reaction.	Solvent.	E_3 .	T° abs.	k_s/k_g exp.	k_s/k_g calc. eqn. (19).
$p\text{-H}_2 + \text{O}_2 \rightarrow o\text{-H}_2 + \text{O}_2$ (a)	H_2O	0	293	1.15	1.31
$2\text{Cl}_2\text{O} \rightarrow 2\text{Cl}_2 + \text{O}_2$ (b)	CCl_4	21,000	338	1.02	382
$\text{C}_2\text{H}_4\text{I}_2 + \text{I} \rightarrow \text{C}_2\text{H}_4 + \text{I}_2 + \text{I}$ (c)	CCl_4	13,000	363	0.2 approx.	424.7

solution. For reaction (b) Hinshelwood and Pritchard point out¹⁹ that in the gaseous phase "the reaction is not a simple change. . . . A sort of average value for E_3 may however be obtained by applying the Arrhenius equation." Likewise in solution the reaction is complex and E_3 varies over the range of concentration. Hence the ratio k_s/k_g may not have the experimental value unity and may be in error by a factor of $e^{-3000/RT}$, which would give results of the right order. Similarly for reaction (c) use is made in the calculation of activation energy of the heat of dissociation of iodine in CCl_4 , which is not known experimentally. In addition E_3 is naturally subject to an error of 1000 cal.

As a further example the calculation of the velocity coefficient of the reaction $\text{Et}_2\text{S} + \text{EtBr} \rightarrow \text{Et}_3\text{SBr}$ may be cited. In $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ the reaction has an activation energy²⁰ of 24,470 cal. and $k = 5.145 \times 10^{-5}$ at 90°C . Values of V and P may be calculated as before, giving $k = 3.11 \times 10^{-3} \text{ sec.}^{-1}$

For more concentrated solutions we may follow the procedure of Wheeler,^{2(f)} who, however, applies his theory to the whole range of concentrations. Fortunately the two methods turn out to be nearly equivalent. The method is very similar to that adopted in section II. In a concentrated solution any molecule of type 1 makes $2\nu_1$ collisions per sec. with the surrounding molecules, and for the n_1 molecules of type 1 per cubic centimetre the total number of collisions is $2n_1\nu_1$. Hence the total number of collisions between molecules 1 and 2 per cubic centimetre per sec. is

$$2n_1\nu_1 \frac{n_2}{n_1 + n_2 + n_s} = \frac{2n_1n_2\nu_1}{n_s} \text{ (approximately)} \quad (20)$$

where n_s is the number of solvent molecules per cubic centimetre. Even in fairly concentrated solution n_s is large compared with n_1 and n_2 .

The artificial selection of one type molecule may be removed by taking the mean of $\nu_1 + \nu_2$. It follows that

$$k = \left(\frac{\nu_1 + \nu_2}{n_s} \right) \frac{N}{1000} \frac{E}{RT} e^{-E/RT} \quad (21)$$

Equations (21) and (15) may be compared by putting $d_1 = d_2 = d_{12} = d$, as a sufficient approximation. Then $k_{15}/k_{21} = \frac{\pi}{3} n_s d^3 \frac{E_2}{RT} \frac{1}{e}$, where the factor e^{-1} enters because in equation (15) $E = (E_3 - E_2) + 5/2 RT$,

¹⁸ Cf. Moelwyn-Hughes, *Acta Physico chim. U.R.S.S.*, 1936, 4, 173.

¹⁹ *J.C.S.*, 1923, 123, 2730; 1924, 125, 1841.

²⁰ Corran, *Trans. Faraday Soc.*, 1927, 23, 605.

whereas for equation (21) $E = E_3 + 3/2RT$, the net exponential factor being the same in each case.

$$\frac{\pi}{6} \cdot d^3 n_s = 0.74, \quad k_{15}/k_{21} = \frac{1.48 \cdot E_2}{RT} e^{-1} = \text{approximately } 2.$$

Hence the two equations are in practice equivalent and we shall therefore use equation (15).

The relation between the diffusion theory and the theory which gives equation (20) may be clarified by a consideration of the recurrence of collisions. If we represent the number of collisions per cubic centimetre per sec. on the diffusion theory by C_d (equation (14)) and if α is the probability of return after a collision, then the total number of collisions is $C_d(1 + \alpha + \alpha^2 + \dots) = C_d/(1 - \alpha)$. If we assume first that no reaction occurs, then this result must equal the number of collisions given by equation (20), (C_u), since this gives the collisions between solvent pairs which are distributed by probability, or $C_u = C_d/(1 - \alpha)$.

Now suppose that a fraction γ of collisions between molecules 1 and 2 lead to reaction, and that α is the same as before. Then the total number of collisions leading to reaction is

$$C_d[\gamma + (1 - \gamma)\alpha\gamma + (1 - \gamma)^2\alpha^2\gamma + \dots] = C_d\gamma/[1 - (1 - \gamma)\alpha],$$

TABLE V.

Reaction.	Solvent.	E_3 .	scale.	obs.
OMe ⁻ + 1 : 2 : 4 - C ₆ H ₃ (NO ₂) ₂ Cl	MeOH	17,450	1.88×10^{12}	1.91×10^{11}
OEt ⁻ + 1 : 2 : 4 - C ₆ H ₃ (NO ₂) ₂ Cl	EtOH	16,760	1.64×10^{12}	1.80×10^{11}
OMe ⁻ + MeI	MeOH	21,180	1.67×10^{12}	1.12×10^{12}
OEt ⁻ + MeI	EtOH	19,490	1.37×10^{12}	2.42×10^{11}
m-4 : xylyloxyde + MeI	EtOH	20,500	1.24×10^{12}	1.58×10^{12}
m-4 : xylyl oxide + EtI	EtOH	19,500	1.28×10^{12}	7.5×10^{11}
m-4 : xylyl oxide + PrI	EtOH	21,700	1.37×10^{12}	9.7×10^{11}
EtI + OEt ⁻	EtOH	20,740	1.51×10^{12}	1.28×10^{13}

since a fraction $1 - \gamma$ does not react at the first collision and, of this, a fraction α collides again, of which a fraction γ reacts, etc. Hence the result according to diffusion, $C_d\gamma$, should be modified by a factor $1/(1 - \alpha + \alpha\gamma)$, or since γ is small, by a factor $1/(1 - \alpha)$. If we compare the chance of escape of a molecule 2 from 1 with the chance of collision we obtain a value of α of the order 0.5, so that no great error will be introduced if the factor for recurrence of collisions be omitted.

The number of bimolecular reactions between molecules is small, and in the majority of examples an ion is present. With small positive ions it is difficult to assess the vibration frequency in solution. However, for larger ions such as anions the conditions are more favourable for the theory, and the dipole atmosphere need not be considered, since the displacements of an ion are small and infrequent. After each jump from one equilibrium position to another the ion may have to wait some time before again escaping from its envelope.

In Table V. are considered some examples of reactions between negative ions and halide molecules, which fulfil the conditions discussed above. Since the parachor and molecular volume of the ions are not accessible the values for the radicals have been used: for large ions the

acquisition of a negative charge by a radical will not greatly affect the radius, and an inspection of the formula shows that the order of the result will not be affected. z has been calculated at 298° K.

The values for z_{obs} are taken from Moelwyn-Hughes¹⁸ except for the last reaction, which has been studied by Williams, Perrin and Gibson,²¹ the calculated value of z is remarkably constant.

IV. The Influence of Pressure on Bimolecular Reactions.

The two different views of bimolecular reactions, gas-collisions and diffusion, are clearly differentiated by the influence of pressure on reaction velocity. On the former view due to Moelwyn-Hughes it is impossible to calculate the influence of pressure on the z factor, and hence attention has been focussed on the effect on the energy of activation.²² Under the high pressures used by Williams, Perrin and Gibson²¹ the influence of p on z is by no means negligible, and may in fact account for the whole of the pressure effect. Thus for the reaction $\text{C}_2\text{H}_5\text{I} + \text{C}_2\text{H}_5\text{O}^-$

these authors find that, at 1 kg. per cm^2 , $k = 1.28 \times 10^{13} e^{-\frac{20,740}{RT}}$ and at 3000 kg. per cm^2 , $k = 2.23 \times 10^{13} e^{-\frac{20,800}{RT}}$, the influence of p on E being negligible.

In order to calculate the pressure effect on z , which alone falls within the scope of this paper, ν must be expressed as in equation (5), since the use of equation (6) would involve the unknown influence of pressure on $[P]$. Equation (5) is, however, dependent solely on volume considerations. We may write

$$z = B(V_1^{\frac{1}{2}} + V_2^{\frac{1}{2}}) \left[\frac{(V_1^{\frac{1}{2}} + V_s^{\frac{1}{2}})^2 A_1}{(V_1^{\frac{1}{2}} - V_{10}^{\frac{1}{2}})} + \frac{(V_2^{\frac{1}{2}} + V_s^{\frac{1}{2}})^2 A_2}{(V_2^{\frac{1}{2}} - V_{20}^{\frac{1}{2}})} \right], \quad (22)$$

where $A_1 = 1/M_1$, $A_2 = 1/M_2$ and $B = 1.186 \times 10^3 E_2 E$ at 25°. Hence

$$\begin{aligned} -\frac{1}{B} \frac{dz}{dp} &= -\frac{1}{B} \frac{dz}{dV} \frac{dV}{dp} = \\ (V_1^{\frac{1}{2}} + V_2^{\frac{1}{2}}) &\left[\frac{2}{3} A_1 \frac{(V_1^{\frac{1}{2}} \beta_1 + V_s^{\frac{1}{2}} \beta_s)(V_1^{\frac{1}{2}} + V_s^{\frac{1}{2}})}{(V_1^{\frac{1}{2}} - V_{10}^{\frac{1}{2}})} - \frac{A_1}{3} \frac{(V_1^{\frac{1}{2}} + V_s^{\frac{1}{2}}) V_1^{\frac{1}{2}}}{(V_1^{\frac{1}{2}} - V_{10}^{\frac{1}{2}})^2} \beta_1 \right. \\ &+ \frac{2}{3} A_2 \frac{(V_2^{\frac{1}{2}} \beta_2 + V_s^{\frac{1}{2}} \beta_s)(V_2^{\frac{1}{2}} + V_s^{\frac{1}{2}})}{(V_2^{\frac{1}{2}} - V_{20}^{\frac{1}{2}})} - \frac{A_2}{3} \frac{(V_2^{\frac{1}{2}} + V_s^{\frac{1}{2}}) V_2^{\frac{1}{2}}}{(V_2^{\frac{1}{2}} - V_{20}^{\frac{1}{2}})^2} \beta_2 \left. \right] \\ &+ \frac{1}{3} \left[\frac{(V_1^{\frac{1}{2}} + V_s^{\frac{1}{2}})^2}{(V_1^{\frac{1}{2}} - V_{10}^{\frac{1}{2}})} A_1 + \frac{(V_2^{\frac{1}{2}} + V_s^{\frac{1}{2}})^2}{(V_2^{\frac{1}{2}} - V_{20}^{\frac{1}{2}})} A_2 \right] (V_1^{\frac{1}{2}} \beta_1 + V_2^{\frac{1}{2}} \beta_2) \quad (23) \end{aligned}$$

where the β 's are compressibilities, i.e., $\beta_1 = -\frac{1}{V_1} \frac{dV_1}{dp}$, $\beta_2 = -\frac{1}{V_2} \frac{dV_2}{dp}$, $\beta_s = -\frac{1}{V_s} \frac{dV_s}{dp}$. V_{10} and V_{20} are assumed to be incompressible, since the main effect of pressure is to close up the vibrations of the molecules, which are absent at 0° abs.

A simplification is achieved by writing $\beta_1 = \beta_2 = \beta_s = \beta$, which is in practice often approximately correct. This gives

²¹ *Proc. Roy. Soc., A*, 1936, **154**, 684.

²² *Cf. Moelwyn-Hughes, Trans. Faraday Soc.*, 1936, **32**, 1723.

$$-\frac{1}{B} \frac{dz}{dp} = (V_1^{\frac{1}{3}} + V_2^{\frac{1}{3}}) \beta \left[\frac{(V_1^{\frac{1}{3}} + V_s^{\frac{1}{3}})^2 (2V_1^{\frac{1}{3}} - 3V_{10}^{\frac{1}{3}}) A_1}{(V_1^{\frac{1}{3}} - V_{10}^{\frac{1}{3}})^2} + \frac{(V_2^{\frac{1}{3}} + V_s^{\frac{1}{3}})^2 (2V_2^{\frac{1}{3}} - 3V_{20}^{\frac{1}{3}}) A_2}{(V_2^{\frac{1}{3}} - V_{20}^{\frac{1}{3}})^2} \right] \quad (24)$$

Hence dz/dp can be positive or negative. The exact points of inflexion can only be obtained by a second differentiation; however, the values of V are sufficiently close to take as criteria $2V_1^{\frac{1}{3}} < \text{or} > 3V_{10}^{\frac{1}{3}}$ and $2V_2^{\frac{1}{3}} < \text{or} > 3V_{20}^{\frac{1}{3}}$. Since for most temperatures employed $2V_1^{\frac{1}{3}} < 3V_{10}^{\frac{1}{3}}$ (or $V_1 < \frac{27}{8} V_{10}$), $\frac{dz}{dp}$ will be positive.

Williams, Perrin and Gibson²¹ give an increase in z from 1 kg. per cm². to 3000 kg. per cm², although it is difficult to assign an exact value for E . We may calculate from their results

$$\frac{dz}{z_{\text{mean}}} = \frac{0.95}{3000 \times 1.75 \times 1000 \times 981} = 1.46 \times 10^{-10}$$

per bar. In order to compare this value with the theoretical result, it is clear that we should use the same formula for dz and z , *i.e.*, z should be calculated from equation (22). This is readily accomplished as far as the term for EtI is concerned, for which $V_0 = 63.93$, from density data. For EtO⁻ we shall take the value calculated from additivity for the radical and reduce it to 0° abs. in the same ratio as for EtOH, giving $V_0 = 40.0$, $V = 61.7$ at 25° C. The result, while approximate, will not be seriously in error, especially since the two terms in equation (24) inside the brackets are of the same order. This gives $z = 1.46 \times 10^{13}$ at 25°. For the compressibility of EtI we calculate from the International Critical Tables, $\beta = 4.63 \times 10^{-11}$, EtOH having practically the same value. Hence $\frac{dz}{z} = 0.574 \times 10^{-10}$ per bar, in satisfactory agreement with the experimental value 1.46×10^{-10} per bar. At higher pressures, 5000 kg. per cm², dz/z is much smaller, but results are less accurate at higher pressures. The other examples given by Williams, Perrin and Gibson, are unsuitable, as they deal with ionic or slow reactions; for the latter allowance must be made for the influence of pressure on equilibrium. It is clear, however, that the effect of the z term is not negligible and may account for about all the pressure change in some cases.

My thanks are due to Mr. Slack for valuable discussions, especially on the question of recurrent collisions.

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THERMODYNAMICS AND THE VELOCITY OF IRREVERSIBLE PROCESSES.

PART II.: CHEMICAL REACTION VELOCITY.

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The application of the theory of fluctuations and the second law of thermodynamics to irreversible processes in the steady state has already been discussed. In the examples referred to,¹ fluctuations in the entropy and available energy of different elements of the system were assumed to be independent of one another. Important changes in the velocity of irreversible processes arise when this assumption no longer holds, as in chain reactions, or in changes occurring in solid systems. The present paper deals with chemical irreversible processes.

Metastability and the Rate of Chemical Change.

A number of assumptions have to be made in order to apply thermodynamic considerations to chemical change. Spontaneous change can only take place in the direction of decreasing free energy or increasing entropy, as the case may be. It is, however, impossible to apply thermodynamic methods unless it is assumed that equilibrium is maintained with respect to infinitesimal fluctuations of concentration (*i.e.*, the pressure remains uniform) and of average translational energy (*i.e.*, the temperature remains uniform). Physico-chemical examples are known where such assumptions no longer hold, as in explosion waves, but in such cases a special kinetic theory has to be applied. Apart from such exceptions, irreversible chemical change has the peculiarity that the system satisfies a thermodynamic criterion for equilibrium $\delta F = 0$ or $\delta S = 0$, and yet undergoes irreversible change. This is due to the fact that local chemical change cannot be expressed even approximately in terms of infinitesimal entropy and free energy changes, but requires a minimum fluctuation ΔS in order to take place at all. In terms of equilibrium theory, the system is metastable with respect to chemical change.

From Boltzmann's theorem, the average probability of such a fluctuation is proportional to $e^{\Delta S/k}$, *i.e.*,²

$$W' = W e^{\Delta S/k},$$

where W is the probability that the element of the system considered shall have the average entropy of the system, before chemical reaction, and W' the probability that the entropy shall depart from this value by ΔS . The use of thermodynamic functions to describe the behaviour of a small number of molecules implies that certain processes of averaging are valid, as is discussed below. When it is justified, the metastability

¹ Ubbelohde, *Trans. Faraday Soc.*, 1937, **33**, 599.

² Cf. Einstein, *Ann. Physik*, 1910, **33**, 1275.

of the system with respect to chemical change implies that ΔS must be negative for a change to take place. This is equivalent to the statement that in order for chemical change to occur in any element it must pass through a less probable transition state, though the ultimate direction of change must be to a more stable state.

If the weighted average of the transition probabilities between the various states in the statistical make-up of the system do not change appreciably with temperature, etc., and if the chemical reaction proceeds as the result of independent fluctuations (see below) the velocity constant μ of the reaction may be assumed proportional to the probability of finding the minimum fluctuation required,

$$\mu = be^{\Delta S/k}$$

where b is a constant. The only thermodynamic restriction on the relation between the reaction rate and such probabilities is that the equation when used to express the condition for dynamic equilibrium must lead to the appropriate thermodynamic formulæ, for example with respect to the activities of the components.

In a balanced action $A_1 + A_2 \rightleftharpoons B_1 + B_2$ dynamic equilibrium between the different molecular species is reached when the velocity of the forward reaction $\mu_1 = b_1 e^{\Delta S_1/k}$ is equal to the velocity of the reverse reaction, so that the equation

$$\mu_1/\mu_2 = 1 = (b_1/b_2)e^{(\Delta S_1 - \Delta S_2)/k}$$

must be equivalent to the law of mass action. This will be the case if the ratio of the constants b_1/b_2 is independent of the activities of A_1 , A_2 , etc., and if the transition state is the same for the forward reaction as for the back reaction. From the definition of entropy, when the transition state is the same $\Delta S_1 - \Delta S_2 = \Delta S_r$, where ΔS_r is the entropy difference between the initial and final states and is independent of the transition state. In order to bring out the connection between the dynamic equilibrium constant and the activities of the various components, it is only necessary to write

$$S = k \ln a + \text{const. per molecule,}$$

from which

$$e^{\Sigma k \ln a} = \text{const.}$$

or

$$\frac{a_1 a_2 \dots}{a'_1 a'_2 \dots} = \text{const.}$$

The expression selected for the velocity constant thus satisfies the thermodynamic criterion for equilibrium, but there is nothing to show that it is the only expression to do so.

If the fluctuations are assumed to be isothermal,² then in the equation

$$T\Delta S_1 = \Delta H_1 - \Delta F_1$$

$$\Delta H_1 = 0 \text{ and } \Delta S_1 = -\Delta F_1/T.$$

The analogy with ordinary equilibrium theory may be pushed further by treating this minimum fluctuation as if it were a molecular species present in very small concentration, and in equilibrium with the rest of the system. This makes it possible to write an equilibrium constant $\ln K = \ln (\text{concentration of requisite fluctuations}) + \Sigma n_i \ln a_i$, where

$$\Delta F = -kT \ln K$$

is the average free energy change in forming a reaction complex. In this way

$$\mu = bK.$$

The advantage of such an analogy is that when it is justified the velocity constant is shown to depend upon any variable x according to the equation

$$\frac{d \ln \mu}{dx} = \frac{d \ln K}{dx} + \frac{d \ln b}{dx} = -\frac{1}{kT} \frac{d\Delta F}{dx} + \frac{d \ln b}{dx}.$$

When x is the temperature, this leads to the Arrhenius equation

$$\frac{d \ln \mu}{dT} = \frac{d \ln K}{dT} = \frac{\Delta E}{kT^2},$$

but any other thermodynamical variable may be selected. For example, if H is the magnetic field, the equations

$$\begin{aligned}\Delta F &= \Delta F_0 - \frac{1}{2} H^2 (\chi' - \chi_0) \\ \frac{d \ln \mu}{dH} &= + \frac{H}{kT} (\chi' - \chi_0) = -\frac{1}{kT} \frac{d\Delta F}{dH},\end{aligned}$$

where ΔF_0 is the requisite fluctuation in the absence of the field, χ' the susceptibility of the transition state, and χ_0 of the system as a whole, indicate that the reaction velocity may be markedly altered in the presence of a magnetic field (either applied externally, or by adding paramagnetic molecules such as NO) if the transition state has a magnetic susceptibility very different from the normal. This may happen in reactions involving aromatic nuclei, or other systems whose diamagnetism includes resonance terms, or on the other hand when the reaction involves paramagnetic free radicals.

Although the constant b cannot be obtained from purely thermodynamic theory, it may be noted that it is intimately connected with the velocity of irreversible processes such as diffusion, or the dissipation of kinetic energy by viscosity in the same systems. These processes correspond with local changes where ΔS is very small, so that the second factor is unity. Although a specific connection may be obtained from the theory of dimensions, the discussion is outside the scope of the present paper.

It must be emphasised that the form of the above equations is not new.³ The purpose of the present discussion is to renew the emphasis on their connection with the theory of fluctuations, and thus with equilibrium theory, and also to discuss the position of chain reactions in the theory of fluctuations.

Chain Reactions.

The method of averaging which is implicit in any thermodynamic treatment of reaction velocity cannot be expected to apply to chemical reactions involving long chains, since in such cases the fluctuations in any element of the system can no longer be treated as independent of that of its neighbours. An expression of the type

$$\mu = bK$$

is based on the Boltzmann Einstein expression for the *average* number of requisite fluctuations to be found in any element. Kinetic theory identifies this with the average number of "active" complexes. It is

³ Moelwyn Hughes, *Trans. Faraday Soc.*, 1936, **32**, 1723; M. Evans and M. Polanyi, *ibid.*, 1937, **33**, 448 and earlier papers; C. N. Hinshelwood, *J.C.S.*, 1937, 635.

important to note, however, that whereas the reaction velocity is determined by the average number of molecules of a particular kind taken over all elements of volume *at any instant*, the kinetic average,

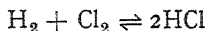
$$\bar{n}_v = (\Sigma n \delta v) / (\Sigma \delta v)$$

the thermodynamic average is the time average in any given element

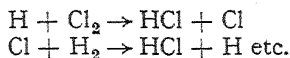
$$\bar{n}_\phi = (\Sigma n \phi) / (\Sigma \phi)$$

where ϕ is the subdivision of the time scale used in averaging. According to the ergodic hypothesis these two averages will be the same, provided the system is observed for a sufficient length of time, *i.e.*, provided $\Sigma \psi$ is sufficiently large.

When equilibrium may depend on a chain reaction, as in



the probability of finding active molecules, or atoms, in any element of the system is no longer independent of the neighbouring elements, nor is it independent of previous history in any one element. In what follows it is convenient to refer to fluctuations which are not independent in space or time as co-operative. At present it is hardly profitable to discuss the more complicated types of interdependence, as in chain branching, from the standpoint of thermodynamics, though in every case the expression for the irreversible reaction velocity must lead to a dynamic equilibrium constant in agreement with thermodynamic theory. The consequences of the simplest type of co-operative fluctuation may be illustrated for the hydrogen chlorine equilibrium, which is assumed for the sake of illustration to depend on a Nernst reaction chain



Once a hydrogen atom has been formed, it will persist for the whole reaction chain, and its presence is confined to a cell whose magnitude depends upon the pressure.⁴ In order to keep the *time average* of the concentration of atoms in accord with the Boltzmann expression, the probability of spontaneous appearance must be correspondingly lowered. Neglecting for the moment the reaction cell effect, the probability of spontaneous appearance bears a simple relation to the average life of a fluctuation. For example, when the fluctuations are independent, this average life depends amongst other things upon the collision frequency. When the fluctuations lead to chain reactions involving n such collisions, the average life of these fluctuations is increased by the factor n , so that the probability of spontaneous appearance of a fluctuation involving a co-operation of n normally independent events will be $1/n$ times the probability of appearance of the single event, in this simple case.

In consequence, the kinetics of chain reactions differ in a number of ways from those of reactions involving independent fluctuations. For example, if a reaction system is suddenly raised to a temperature at which a simple reaction with the same activation energy would proceed, the chain reaction may show a kind of metastability or reluctance to start if n is at all large. Actually this behaviour is seldom observed, owing to the rôle of the walls in starting chains by a different set of fluctuations from those determining equilibrium in the gas. Again, the velocity of chain reactions is usually larger than those of simple

⁴ Ubbelohde, *Nature*, 1933, 131, 328.

reactions requiring fluctuations of the same magnitude, though this can only happen when the chains start from the walls or in some other way not thermodynamically connected with the large chain length.

The dependence of chain reactions on pressure is usually quite different from that of simple reactions. This is again due to the fact that the fluctuations leading to local chemical reaction are not independent. Kinetic theory is more suitable than thermodynamic theory in discussing the complicated dependence on pressure actually observed. The only general statement which can be made is with regard to the reaction cell effect. After τ collisions any chain is confined to a cell whose volume is proportional to

$$r^{3/2}/\rho^3$$

where ρ is the density. It follows that the degree of interdependence of fluctuations in different elements of volume decreases with rise of pressure, so that all chain reactions must approximate in velocity to simple reactions as the pressure increases. This tendency may sometimes be obscured by technical difficulties in maintaining isothermal conditions at high pressures.

For the sake of brevity, no discussion will be made of the assumptions about the transition state which lead to more detailed results than the above. The essential points of the present theory are that a system in which chemical reaction proceeds at a finite rate, and in which the temperature and concentration remain uniform, must be metastable with respect to chemical change, *i.e.*, require fairly large local fluctuations for chemical change to occur. When the concentration of these fluctuations is treated from the standpoint of mass action theory, then provided they are independent of one another, the equation for the velocity constant $\mu = bK$ which is obtained may be differentiated with respect to any thermodynamic variable according to the usual formulæ. When they are not independent however, as in chain reactions, the thermodynamic treatment of reaction velocity becomes too complicated to be really useful. It may be pointed out that there are important analogies between such co-operative fluctuations in chemical reactions, and the velocity of irreversible processes in solids. The essential feature of co-operative systems is that the kinetic average may show large departures from the thermodynamic average.

Summary.

Irreversible chemical change is characterised by the fact that although the system is in equilibrium with respect to temperature and pressure, chemical reaction can only take place as the result of local fluctuations of sufficient magnitude. When these fluctuations can be treated as independent, the velocity constant can be expressed in terms of an equilibrium constant for their concentration, and this equilibrium constant changes with changes in the thermodynamic variables of the system, in accordance with the usual formulæ. When they are not independent, wall effects and an anomalous dependence of the velocity of reaction upon pressure may be expected, as is observed for chain reactions. In general thermodynamic probabilities, even in a system at constant temperature and pressure, can only be used to express the velocity of irreversible change in the system, when they are proportional to kinetic probabilities, and do not depend on co-operative fluctuations.

PART III. CHANGES OF STRUCTURE IN SOLIDS.

The object of this paper, as in the other examples considered,¹ is to discuss what information is available from thermodynamic considerations on the rate of change of functions such as S and F in solids. In chain reactions, the co-operative factor for fluctuations leading to irreversible change seldom falls below 10^{-6} , whereas in solids a change in S or F may depend on the co-operative behaviour of a large number of molecules at the same instant. As a result, the existence of metastable states and the phenomenon of hysteresis are fairly common, and the ergodic hypothesis does not correspond with experimental observations, unless it is framed so as to exclude co-operative changes, or to cover very large periods of observation.

Solid-Liquid Transitions.

The most familiar example of a co-operative change is the transition from solid to liquid, or vice versa. Closely similar phenomena of hysteresis are observed whether the liquid phase is a melt or a solution. The main experimental features may be summarised as follows:—

Superheating.—It is never possible to heat a solid above the melting-point without melting taking place, except that the temperature of the as yet unmolten solid may temporarily rise above the melting-point whilst melting proceeds.

Supercooling.—If a liquid is cooled below the melting or saturation point, crystallisation always proceeds if solid nuclei are present, though these only grow at a finite rate. In the absence of nuclei a liquid may be cooled well below the transition point without the appearance of solid. It is important to note that the supercooled melt or solution satisfies all the thermodynamic criteria for equilibrium, for example, with respect to uniformity of temperature, pressure and concentration throughout the liquid phase, equilibrium with the vapour phase, velocity of chemical change in solution, etc., but can remain for very long periods without the appearance of solid.

The Rule of Successive States.—This rule, which is generally though not universally obeyed in irreversible changes, states that in spontaneous crystallisation the least stable crystalline form appears preferentially. The same rule applies to crystallisation from the vapour phase.

These observations, which summarise a great deal of experimental work, are readily interpreted in terms of the usual thermodynamic equations and the theory of fluctuations. The free energy of the liquid per unit mass may be written

$$F_L = H_L - TS_L$$

and of the solid

$$F_S = H_S - TS_S$$

so that

$$F_L - F_S = (H_L - H_S) - T(S_L - S_S).$$

The heat content of the solid is smaller than that of the liquid, but owing to the greater order of the solid its entropy S_S is likewise smaller

¹ Ubbelohde, *Trans. Faraday Soc.*, 1937, **33**, 599, and Part II.

² Tamman, *Aggregatzustände*, Leipzig, 1922, 217.

than S_L . In consequence, spontaneous solidification does not become thermodynamically possible till the temperature falls below a transition point T_M , thus making the second term sufficiently small to give a positive value to

$$F_L - F_S$$

and thus to give rise to a decrease of free energy for the spontaneous change from liquid to solid. Nevertheless, even when the change is thermodynamically possible the rate at which it takes place may be so slow as to make it negligible, compared with the rate of irreversible processes such as diffusion, or the dissipation of kinetic energy by viscosity, in the same system.

When thermodynamic functions are used to evaluate the probability of a spontaneous change from liquid to solid, allowance has to be made for the different methods of averaging proper to thermodynamic and kinetic calculations. Thus owing to the fact that there is an entropy decrease on solidification, and that no difference between solid and liquid can be specified unless a minimum number of atoms n is considered at the same time, the thermodynamic probability of finding the requisite fluctuation is of the form $W' = We^{n\Delta S/k}$ where ΔS may be equated to the average entropy change on solidification per molecule; if the change from solid to liquid involves a transition state, ΔS refers to the entropy difference between the initial and transition states.

The velocity of spontaneous change is, however, governed by the kinetic probability of finding the requisite fluctuation. Owing to the fact that the minimum number of atoms n must be neighbours, and in some cases must have special configurations (especially in complex crystal structures) the probability that n neighbouring atoms shall have the same thermodynamic probability change ΔS at the same instant is very considerably smaller than if they can be selected at random throughout the volume considered. In other words, the kinetic probability of finding a nucleus involves co-operative fluctuations of the system, and just as in the case of chain reactions this leads to a lengthened life of the nucleus when once formed, and to a smaller probability of its spontaneous appearance than is suggested by the thermodynamic factor. A concrete example of the co-operative factor is discussed below, but owing to its varied character it is more convenient to write the rate of change of thermodynamic functions of the system, which involve a co-operative change, as proportional to

$$fe^{n\Delta S/k}$$

where f is the co-operative factor. When the minimum number of molecules required to specify the change of phase is large, or when the co-operative factor is large owing to a complicated crystal structure, the liquid may remain in metastable equilibrium for days, with respect to the fluctuations producing the solid, and yet be in complete equilibrium with respect to infinitesimal fluctuations of pressure, concentration, etc. It may be noted that a separation of the kinetic probability of change into a term dependent upon the thermodynamic probability change, $e^{n\Delta S/k}$, and the co-operative factor f , when this is permissible, leads to definite conclusions about the velocity of irreversible change without a precise knowledge of the kinetic factor. The only thermodynamic restriction on expressions for the kinetic probability of change is that they must lead to a dynamic equilibrium with the same

dependence on the thermodynamic functions of the system as is given by the theory of fluctuations. Other expressions for the kinetic probability of change are not excluded provided they satisfy this restriction.

The significance of the rule of successive states is readily seen in the light of this simple expression. The solid phase most likely to appear spontaneously is that for which the expression $f e^{n\Delta S/k}$ is as large as possible. Neglecting for the moment the effect of f , the solid structure with the smallest entropy difference from that of the liquid will appear preferentially. If the fluctuations are treated as isothermal³

$$\Delta F = -T\Delta S$$

and the solid whose free energy approximates most closely to that of the liquid will appear preferentially. This is, of course, the solid with the largest free energy, *i.e.*, the least stable. Exceptions to the rule may arise when the co-operative factors differ very appreciably for two competing crystal structures.

Rôle of Surface Processes in Supercooling and Superheating.

A very important peculiarity of co-operative changes in solids arises as follows: When a nucleus is present in a change of phase, it has the possibility of growing at the expense of the rest of the medium as the result of fluctuations at the surface of separation. By this means it is possible to switch from an irreversible process depending on the co-operation of molecules in three dimensions, to a process requiring co-operation in two dimensions only, and involving a much smaller number of atoms at any instant. Both the co-operative factor and the entropy factor are thereby lowered at least to the extent of $(f e^{n\Delta S/k})^{\frac{1}{2}}$, though the ratio of co-operative fluctuations in three and two dimensions is almost certainly even smaller. Its numerical effect may be illustrated, making use of the fact that the time of half-change in a reaction is inversely proportional to the velocity constant. If the two-dimensional co-operative change from liquid to solid takes one hour, the three-dimensional process in the absence of nuclei would take at least two days. The experiments of Volmer⁴ show that even the growth of crystals, from vapour deposited on the surface, which is probably a two-dimensional process, is considerably slower than the velocity of condensation.

Two further points may be noted in connection with these formulæ. In the first place, the extent of supercooling which can be observed in a system will depend (1) On the velocity of irreversible processes dependent on microfluctuations, such as diffusion or viscosity, and (2) On the thermodynamic probability or entropy factor. A comparison of systems in which these two factors are approximately the same, but the tendency to supercooling and the formation of glasses differs, shows that the co-operative factor may likewise be of great importance, particularly when the crystal structure is complex.

Furthermore, a solid does not change explosively into a liquid at the melting-point, as might follow from the Lindemann theory of melting. Melting at the surface takes place much more easily than the spontaneous formation of pockets of liquid in the crystal, owing to the

³ Cf. previous papers and Einstein, *Ann. Physik*, 1910, 33, 1275.

⁴ Volmer, *Z. Physik*, 1921, 5, 31, 188; 7, 1, 13.

much smaller co-operative factor required for two-dimensional fluctuations of the molecules.⁵

Number of Nuclei at Different Temperatures.

The thermodynamic significance of a transition point is primarily that the free energy of the solid in bulk becomes smaller than that of the liquid, so that the solid is more stable than the liquid below the transition point, and is formed at a rate governed by the spontaneous fluctuations in the system. The effect of changes in the thermodynamic variables on the probability of such fluctuations may be discussed in the usual way. For example, as a general rule

$$C_P (\text{liquid}) = T \frac{dS_L}{dT}$$

is larger than

$$C_P (\text{solid}) = T \frac{dS_S}{dT}$$

so that the temperature coefficient of entropy change

$$\Delta S_M (\text{liquid-solid}) = S_{\text{Solid}} - S_{\text{Liquid}}$$

may be written

$$T \frac{d(\Delta S)}{dT} = C_P (\text{solid}) - C_P (\text{liquid}) = \Delta C_P$$

which is negative.

For small changes in temperature ΔC_P may be treated as constant, and

$$\Delta S = \Delta S_M + \Delta C_P \log T/T_M.$$

The entropy factor for the supercooled liquid below a transition point thus becomes

$$e^{n\Delta S/k} = \left(\frac{T}{T_M}\right)^{n\Delta C_P} e^{n\Delta S_M/k}$$

where ΔS_M refers to the entropy change at the melting-point, per molecule. For small differences $\Delta T = T - T_M$ this may be expanded by the binomial theorem to give the entropy factor at a temperature T

$$e^{n\Delta S_M/k} \left(1 + \frac{\Delta T}{T_M} \cdot \frac{n\Delta C_P}{T_M}\right).$$

Since ΔC_P is negative, this result implies that over short ranges of temperature the number of nuclei increases linearly with falling temperature, as observed by Tamman.² As the temperature falls, however, the velocity of irreversible processes such as diffusion decreases in the liquid. The net rate of formation of fresh nuclei at first increases and then decreases again as the result of these two opposing tendencies.

It may be noted that the above formula for the number of nuclei at any temperature does not suggest any essential discontinuity at the transition point. This seems to agree with some experiments quoted by Tamman on preheating a liquid phase and then suddenly cooling it below the transition point. The number of nuclei to appear corresponds with the temperature of preheating, though owing to the relatively long life of a nucleus the system has to be maintained for some time at this temperature to reach equilibrium.

⁵ For a somewhat different view of surface melting, cf. Lennard-Jones, *Trans. Faraday Soc.*, 1931, 354.

Transitions in a Single Phase. Example of a Co-operative Factor.

A number of structural changes in solids are known which take place without change of phase, but which involve the co-operation of a large number of atoms or molecules. Such systems may show metastability with regard to free energy and entropy changes involving a change in the co-operative energy, even though they are in equilibrium with respect to microfluctuations such as lead to the establishment of vapour pressure equilibrium, equality of concentration throughout the solid and so on. Typical examples are listed below. A case for which fairly simple statistical calculations have been made is the transition from an ordered to a disordered solid solution.⁶ The origin of the co-operative factor may be illustrated as follows. In a partly ordered solid solution, the A and B atoms will interchange positions at a rate which is comparable with the velocity of diffusion of atoms through the lattice. Any single interchange will have a probability of the form $ae^{-E/kT}$. Although a purely kinetic theory of the rate of change of order is necessarily rather complicated, the following considerations illustrate how any co-operation between molecules slows down the velocity of change.

Experiment suggests that any co-operative system is divided into domains, such that the degree of order, etc., in any one domain is without influence on that in the neighbouring domains. If the average number of molecules in any domain is $2N$, then the probability of a change of order as a result of a single A — B interchange is not simply

$$ae^{-E/kT}, \text{ but } ae^{-E/kT} (1 - ae^{-E/kT})^{N-1}$$

since it is necessary to specify that all the other atoms do not interchange in the interval considered. Similarly the probability of change as the result of interchange of two pairs is

$$a^2e^{-2E/kT} (1 - ae^{-E/kT})^{N-2}$$

the average interchange of significance for the state of order is \bar{n} molecules, where \bar{n} is proportional to

$$\sum_r r \cdot [a^r e^{-rE/kT} (1 - ae^{-E/kT})^{N-r}].$$

The average interchange neglecting any considerations of the other molecules in the same domain would be

$$\sum_r r [a^r e^{-rE/kT}].$$

Although these kinetic expressions do not apply where \bar{n} is at all large, owing to the fact that the activation energy E depends on the number of atoms already in the ordered state, they illustrate the general feature of co-operative systems, that the rate of spontaneous change is smaller than would be expected from the thermodynamic factor. The magnitude of this factor may be estimated in this instance, since when the solid is suddenly lowered in temperature by ΔT the entropy fluctuation required to reach equilibrium is $\Delta S = 2NC_0\Delta T/T$, where C_0 is the additional specific heat due to the change in order, per molecule. At the present time no satisfactory way of calculating N in various co-operative

⁶ Bragg and Williams, *Proc. Roy. Soc., A*, 1935, **152**, 231.

systems is available. A certain amount of evidence is available from the size of crystal mosaics, the magnitude of Barkhausen jumps in ferromagnetic substances subjected to an external field, or the change in electrical resistance on forming an ordered from a disordered phase. Estimates may also be made from the extent to which any system shows hysteresis.

Hysteresis and the Breakdown of the Metastable State.

A system showing hysteresis is metastable with respect to co-operative fluctuations involving large numbers of molecules, but is stable with respect to microfluctuations such as are associated with temperature and concentration equilibrium. Thermodynamically, hysteresis may be characterised by the statement that the value of any variable χ related to the co-operative portion of the free energy has to be varied by a finite amount before the system adjusts its free energy to the change in the variable.

Since

$$\Delta S = (\Delta H - \Delta F)/T$$

the failure of the system to adjust its free energy to a change in χ means that the free energy in the metastable state is too large by

$$\frac{\partial F}{\partial \chi} \cdot \Delta \chi + \frac{1}{2} \frac{\partial^2 F}{\partial \chi^2} \cdot \Delta \chi^2 + \dots$$

ΔH as a rule is little affected, so that the metastable state decreases in entropy, and the fluctuation required to reach to equilibrium increases in probability as χ increases, until the metastable state breaks down and the system adjusts itself to a lower free energy.

It is interesting to note that in a transition of the second kind $\frac{\partial F}{\partial \chi}$ and $\frac{\partial^2 F}{\partial \chi^2}$ may be equal to zero. In this case the breakdown of a metastable state depends on the growth of the function $\frac{\partial^3 F}{\partial \chi^3} \cdot \frac{\Delta \chi^3}{6}$ which changes much more steeply with a change in $\Delta \chi$ and may lead to sharp hysteresis loops.

In the absence of a suitable theory of the size of domains in co-operative systems, it is convenient to consider a brief survey of the hysteresis observed in various co-operative changes:—

<i>Type of Change.</i>	<i>Variable.</i>	<i>Hysteresis.</i>
Free energy of ferromagnetics in an external field.	Field strength	Large at ordinary temperatures for polycrystalline material.
Spontaneous magnetisation energy of ferromagnetics.	Temperature.	Small for pure metals at Curie point, large for alloys with structure change at the Curie point.
Crystallisation.	Temperature.	Large when structure is complex or viscosity high.
"Rotation" in crystals.	Temperature.	Appreciable (0.3°) for NH_4Cl .
Formation of β - from α -phase in palladium hydride.	Pressure of hydrogen.	Large, especially at low temperatures.
Disordered \rightarrow ordered phase in alloys.	Temperature.	Appreciable.
Superconducting state of metals.	Temperature.	Appreciable relaxation time effects.

⁷ Justi and v. Laue, *Physik. Z.*, 1934, **35**, 945.

The thermodynamic theory of irreversible change throws some light on all these instances. For ferromagnetic substances, the fact that pure metals may show appreciable hysteresis at ordinary temperatures with respect to field strength, but show practically no hysteresis with respect to temperature at the Curie point, is due partly to the decrease in size of domains at higher temperatures, partly to the greater velocity of irreversible change at high temperatures. The hysteresis is large for alloys which show a change of structure at the Curie point, simply because the breakdown of the metastability depends on volume changes which have a larger co-operative factor than for pure metals.

The hysteresis in the ammonium chloride transition has been described by Smits and MacGillavry.⁸ An analogous hysteresis is known for the transition in methane.⁹ Both are fairly small. The hysteresis in the formation of the β -phase from the α -phase in palladium hydride has been described by a number of authors.¹⁰ Hysteresis in the order-disorder transformations has been described, *e.g.*, by Johansson and Linde.¹¹ The only points requiring special discussion are the total free energy dissipated in a hysteresis cycle, and the thermodynamic aspects of superconductivity.

Free Energy Dissipation in a Hysteresis Cycle.

The hysteresis observed in different co-operative changes in solids has its effect on a number of properties, such as heat content, specific volume, infra red absorption, dielectric constant, etc. It is perhaps unnecessary to emphasise that with a view to interpreting hysteresis from the standpoint of the thermodynamic theory of irreversible change, the most suitable information is obtainable from a plot of the free energy or entropy of the system against the parameter whose variation leads to hysteresis. In order to illustrate how hysteresis may vary with temperature, for example, in the system hydrogen/palladium, a plot of the entropy of each portion of hydrogen added has been made, against the concentration in the solid phase. If the solid returns to its original condition on removal of the hydrogen,¹⁰ the total entropy increase in a hysteresis cycle must be given by the area of the loop. The results are as follows:—

Tempr.	376° K	433° K	453° K	473° K	573° K
Entropy units/cycle/gm. atom Pd (cals./deg.)	0.56 and 0.52 *	0.27	0.16	0.11	0.00

In this example, the marked hysteresis observed, in spite of the free diffusion of hydrogen through the solid, is probably connected with the fact that the sudden expansion in lattice accompanying the change from the α - to the β -phase requires a co-operative energy increase of the palladium atoms. There is a further possibility that the β -phase may be ordered or disordered at the same temperature, though this cannot be verified directly owing to the low scattering power of hydrogen for

⁸ A. Smits, *Physik. Z.*, 1934, **35**, 914.

⁹ Eucken and Bartolomé, *Göttinger Nachrichten*, 1934, 51-64.

¹⁰ Ubbelohde, *Proc. Roy. Soc., A*, 1937, **159**, 295.

¹¹ Johansson and Linde, *Ann. Physik*, 1928, **86**, 291.

* According to mode of addition.

X-rays. Similar plots in other co-operative systems indicate how much the free energy must be increased before the metastability breaks down.

Superconductivity and the Application of the Heat Theorem to Irreversible Change.

From the Gibbs-Helmholtz equation

$$F - H = T \frac{dF}{dT}$$

and the hypothesis of Nernst

$$\lim_{T \rightarrow 0} \frac{\partial F}{\partial T} = 0,$$

it is clear that the quantities F and H tend to equality at low temperatures. Since F must be measured in a reversible process, whereas H may be measured in any process whether reversible or irreversible, a natural extension of the Nernst Heat Theorem would seem to be that *the probability of irreversible changes must tend to zero as the temperature tends to zero*. This is connected with the fact that the fluctuations in a system tend to zero with falling temperature.

In the case of the spontaneous decrease of available electrical energy, the dissipation of such energy might be expected to decrease as the temperature falls. From the thermodynamical standpoint, the only special feature about superconducting systems is that the change to a negligible rate of dissipation is abrupt. Even in the absence of other information, the analogy with other systems leads to the hypothesis that some form of co-operative energy becomes significant for the conduction electrons below a transition temperature. This must appear from the specific heat anomaly always connected with such changes.¹² Ordinary statistical methods of calculating the rate of dissipation of available energy (*i.e.*, the electrical resistance) assume that it can be calculated in terms of the fluctuations of the individual electrons. The essential feature is, however, that as in other co-operative systems an irreversible change involving a co-operative parameter can only be expressed in terms of the fluctuations of the system (or its domains of co-operative influence) taken as a whole.

From this it follows that it must be as difficult to increase the induction energy associated with a superconducting solid by increasing the external magnetic field, as it is for the energy to decrease spontaneously. The anomalous permeability of a superconducting solid is well known.¹³ The superconducting solid can, however, dissipate electrical energy once it is acted on by a threshold magnetic field H . This minimum field can be calculated on the assumption that it must be at least large enough to permit micro-fluctuations in the system, *i.e.*, it must at least be sufficient to wipe out the free energy difference between the superconducting and the nonsuperconducting state. With smaller fields than this, the electrons would still have to overcome a certain amount of co-operative free energy, a much less probable event, especially at low temperatures. (The change might, however, be expected to take place slowly for fields just below the threshold value.)

¹² Ubbelohde, *Introduction to Modern Thermodynamical Principles*, Oxford, 1937.

¹³ Meissner, *Physik. Z.*, 1934, **35**, 931.

If the specific heats in both the superconducting and nonsuperconducting states are assumed independent of the field strength, the free energy difference between the superconducting and nonsuperconducting solid at a temperature $T_1 - T_0$ below the transition point T_0 will be

$$\Delta F_i = \Delta H - T\Delta S = \int_{T_1}^{T_0} (C_s - C_0) dT - T \int_{T_1}^{T_0} \frac{(C_s - C_0)}{T} dT,$$

where ΔF_i is the free energy difference per unit mass, which is of course, zero at the transition point, and C_s is the specific heat of the solid per unit mass in the superconducting state, C_0 in the nonsuperconducting state.

The energy of a solid per unit volume in a magnetic field of strength H is $\mu H^2/8\pi$, where μ is the permeability, and the shape of the solid is selected so as to minimise demagnetisation effects. The energy per unit mass is thus $\mu H^2/8\pi\rho$ and the difference of free energy between the superconducting and nonsuperconducting solids in a magnetic field H will be

$$\Delta F_M = (\mu_s - \mu_0) H^2/8\pi\rho.$$

If $\mu_s = 0$ (Meissner) the minimum field which will permit the system to dissipate electrical energy by microfluctuations will be given by the formula (since $\mu_0 \sim 1$)

$$H^2/8\pi\rho = \int_{T_1}^{T_0} (C_s - C_0) dT - T \int_{T_1}^{T_0} \frac{(C_s - C_0)}{T} dT.$$

This equation was first deduced by Gorter and Casimir.¹⁴ It may be noted that analogy with other co-operative systems suggests that this minimum field may have to be exceeded in some cases, in order to break down a metastable state. This is apparently the case for the superconducting alloys, but until more is known about the thermal and electromagnetic properties of these alloys no definite conclusion can be reached. A point of interest is that the rest resistance due to the alternation of different ions in the lattice vanishes below the transition point, so that in this instance the analogy of the Nernst Heat Theorem is completely followed.

From the standpoint of the thermodynamic theory of the velocity of irreversible change, the relaxation effects in the neighbourhood of the transition point¹⁵ may lead to valuable information when more abundant data are available, since they give a clue to the extent of co-operation between electrons.

Summary.

The thermodynamic theory of spontaneous change is applied to the velocity of irreversible changes in solids, in which the thermodynamic functions depend on the co-operative behaviour of a large number of molecules.

In the solid/liquid transition, the phenomena of supercooling, superheating, and the law of successive states are explained in terms of a simple expression for the probability of finding the requisite fluctuations in the system; the same expression leads to a formula for the number of nuclei at different temperatures.

¹⁴ Gorter and Casimir, *Physica*, 1934, 1, 306.

¹⁵ Keesom and van Laar, *ibid.*, 1936, 3, 173.

Particular emphasis is laid on the phenomenon of hysteresis, which must be exhibited to some extent in spontaneous changes in any co-operative system. Typical examples are observed for ferromagnetism, the liquid/solid transition, rotation in crystals, formation of the β - from the α -phase in palladium hydride, and of ordered from disordered structures in alloys.

The thermodynamic aspects of superconductivity in metals are also discussed, since from this standpoint a finite electrical resistance is equivalent to the possibility of a spontaneous decrease of available electrical energy. Although a consideration of Nernst's Heat Theorem suggests that all irreversible changes become less probable towards absolute zero, superconducting metals show an abrupt change below a transition temperature. By analogy with other co-operative systems, the simplest explanation is that some form of co-operative energy becomes important below the transition point. Owing to the fact that spontaneous change is much less probable when it depends on co-operative fluctuations, a metal in the superconducting state shows a reluctance both to increase or decrease its available energy spontaneously, *i.e.*, it shows an anomalous permeability, and no tendency to dissipate its available energy spontaneously as heat. It is, however, possible, as in other co-operative systems, to change the probability of spontaneous fluctuations by changing the variables, in this case by applying a magnetic field. The minimum field required to permit the dissipation of energy by spontaneous fluctuations may be calculated on certain simple assumptions about the system, leading to the equation of Gorter and Casimir.

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REFRACTIVE INDICES OF ANILINE-*o*-CHLOROPHENOL MIXTURES: AND THE NATURE OF THE MOLECULAR COMPOUND.

By C. D. ELLYETT.

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It has been found that change in the degree of association of an associated liquid does not alter the molar refractivity, and from this it has been argued that association does not involve an electronic link, but is merely dipole combination. The evidence that has been obtained where molecular compound formation occurs, however, is much more uncertain. If definite negative results could be obtained, the above idea would appear to be supported; but other work shows that combinations of this type are probably electronic, and so doubt would be cast on the soundness of the refractivity argument. To test this point the molar refractivities of aniline-*o*-chlorophenol mixtures were obtained.

Experimental.

Measurements of refractive index were made with an Abbe Refractometer. A fairly rapid stream of water, constant to within $1/10^\circ$ C., flowed through the instrument; and an electric lamp of 150 c.p. was used as the source of light, the compensator giving readings equivalent to the NaD wavelength. Reproducible values were not obtained unless the

mixtures were weighed in dry air. For this purpose two U-tubes with glass taps were joined together by replacing two of the taps with a wide ground glass joint, so that the two tubes were parallel to each other. The liquids were run in separately into one tube without coming into contact with the open air, and the other tube contained P_2O_5 . Three weighings gave the exact composition of the mixture, which was then run straight into the refractometer. Several readings were taken at different temperatures for each mixture, and the reading at the required temperature read off from a graph.

Results.

Twenty-five different samples of aniline were measured, and the refractive indices were found to lie on a straight line over the range 10° - 40° C., given by $n_D^{20} = 1.5866$; $dn/dt = 0.000545$ per degree. The only reliable values for the physical constants of *anhydrous* aniline are those of Applebey and Davies.¹ Their value at 20° C. agrees with the above value within 0.00025, but they give the temperature coefficient as $dn/dt = 0.00030$, so that results at all other temperatures deviate markedly from the author's values. It appears as if their temperature coefficient must be in error, as the earlier published values, although all somewhat low, due probably to absorption of moisture, agree roughly with a temperature coefficient $dn/dt = 0.000545$.

Similarly, many results were obtained for anhydrous *o*-chlorophenol, the values again lying on a straight line over the range 5° - 45° C., given by $n_D^{20} = 1.5602$; $dn/dt = 0.000555$ per degree. The value $n_D^{40} = 1.5473$, given in the International Critical Tables, corresponds to a liquid which is far from anhydrous. In a very recent paper Burnham and Madgin² give a value $n_D^{40} = 1.5491$, which is in good agreement with the author's value of 1.5492 at this temperature.

The results for the binary mixtures are given in Table I., where n is the refractive index. These values when plotted give a smooth curve markedly concave to the concentration axis.

Discussion of Results.

There are three possible explanations of the linkage in mixtures of this type, *viz.* :—

1. Dipolar association.
2. Electronic or Resonance linkage.
3. Ionic linkage.

(1) The Evidence for a Dipole Association.

Smyth and his co-workers³ arrived at the conclusion that if association involved a definite electronic link, then change in the degree of association brought about by change of temperature or concentration would alter the electronic polarisation (molar refraction) as much as 0.2 to 0.5. As dilution of alcohols with heptane gave a constant value for the molar refraction, which agreed with the calculated additive value, it was concluded that dipole forces were sufficient to account for the observed phenomena. Later workers, with other binary mixtures containing an associated component, arrived at the same conclusion as Smyth.

Where compound formation occurs, however, there is less evidence, and the work that has been done appears to support a slight change in

¹ *J.C.S.*, 1925, 127, 1836.

² *Ibid.*, 1936, 789.

³ *J.A.C.S.*, 1929, 51, 1736.

the molar refractivity.⁴ Trew⁵ considers from graphical evidence that acetone—bromoform mixtures exhibit a real deviation. These results have been recalculated by Smyth's method, and the results for aniline—*o*-chlorophenol have also been calculated in the same way.

The Lorentz-Lorenz expression for a binary mixture is

$$P_{Eab} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{c_a M_a + c_b M_b}{d},$$

where c_a , c_b are the mol. fractions, and M_a , M_b the molecular weights, respectively, and P_{Eab} the electronic polarisation of the mixture. The mixture law is simply

$$P_{Eab} = c_a P_{Ea} + c_b P_{Eb} = P_{Ea} + c_b (P_{Eb} - P_{Ea}).$$

where P_{Ea} and P_{Eb} are the electronic polarisations of the pure constituents. According to Smyth the two expressions should agree within experimental error.

Table I. sets out the results for aniline—*o*-chlorophenol, calculated from the densities and refractivities at 20° C.; and Table II. the results for acetone—bromoform, from Trew's figures at 25° C.

TABLE I.—($P_{Ea} = 30.592$, $P_{Eb} = 33.217$, $P_{Eab} = 30.592 + 2.625 c_b$,
TEMPERATURE 20° C.)

Mol. Fraction <i>o</i> -chlorophenol, c_b .	n .	d .	P_{Eab} (additive).	P_{Eab} (obs.).	Difference.
0.00000	1.5866	1.0218	30.592	(30.592)	0
0.07043	1.5858	1.0423	30.777	30.759	— 0.018
0.12421	1.5851	1.0574	30.918	30.895	— .023
0.27430	1.5829	1.0992	31.312	31.243	— .069
0.40874	1.5806	1.1330	31.665	31.616	— .049
0.49298	1.5787	1.1526	31.886	31.856	— .030
0.54199	1.5776	1.1635	32.015	32.001	— .014
0.59880	1.5759	1.1761	32.164	32.150	— .014
0.72204	1.5718	1.2011	32.487	32.493	+ .006
0.80781	1.5685	1.2175	32.712	32.719	+ .007
0.90772	1.5641	1.2355	32.975	32.973	— .002
0.96831	1.5617	1.2459	33.134	33.139	+ .005
1.00000	1.5602	1.2512	33.217	(33.217)	0

The extent of departure of the molar refractivity from the additive relationship, as given in the last column of Table I., is no greater than the experimental error. Smyth obtained differences of about the same magnitude for alcohol—heptane mixtures, and so these results apparently support his argument. The values given by Trew for the experimental molar refraction (Column V, Table II.) appear to have been calculated inaccurately, and have been recalculated (Column VI.). Column VII. gives the differences between the additive and found values from Trew's figures, and Column VIII. the differences from the recalculated values. These latter differences are smaller in all except two cases, but on the whole are slightly larger than the aniline—*o*-chlorophenol differences. As Trew's density figures are only given to the third decimal place, a

⁴ J.A.C.S., 1932, 54, 2398.

⁵ Trans. Faraday Soc., 1932, 28, 509.

somewhat larger experimental error is to be expected. The acetone—bromoform deviations are certainly all negative, but they are very irregular, and do not show the existence of a definite deviation. *o*-chlorophenol is not a very good liquid to use for this test, as it is probably intramolecularly associated with the same type of link as is used to form the compound; but the acetone—bromoform mixtures show definitely that compound formation does not affect the molar refraction to a greater extent than the magnitude of the experimental errors.

TABLE II.—($P_{E_{\text{acet}}} = 16.186$, $P_{E_{\text{Br}}} = 29.809$, $P_{E_{\text{acet-Br}}} = 16.186 + 13.623 \text{ } \epsilon_{\text{Br}}$, TEMPERATURE 25°C.)

I. Mol. Fraction CHBr_3 .	II. n .	III. d .	IV. $P_{E_{\text{a-Br}}}$ (additive).	V. $P_{E_{\text{a-Br}}}$ (Trew).	VI. $P_{E_{\text{a-Br}}}$ (recalc.).	VII. Differences (Trew).	VIII. Differences (recalc.).
0.0000	1.35657	0.7847	16.186	16.21	(16.186)	0	0
0.0969	1.38342	1.024	17.506	17.54	17.539	—0.034	—0.033
0.2014	1.41143	1.270	18.930	19.40	19.023	—0.470	—0.102
0.2727	1.43046	1.438	19.901	19.99	19.979	—0.089	—0.078
0.4280	1.46887	1.784	22.017	22.08	22.066	—0.063	—0.049
0.4952	1.48558	1.931	22.932	22.98	22.937	—0.048	—0.005
0.5974	1.50838	2.127	24.324	24.43	24.453	—0.106	—0.129
0.6766	1.52637	2.283	25.493	25.52	25.531	—0.117	—0.128
0.7997	1.55251	2.507	27.080	27.23	27.138	—0.150	—0.058
0.9166	1.57705	2.720	28.673	28.82	28.819	—0.147	—0.146
1.0000	1.59445	2.879	29.809	29.80	(29.809)	0	0

These results, however, do not necessarily prove Smyth's argument. In the first place an electronic link may not introduce as great a reduction as 0.2 to 0.5 in the molar refraction. Especially may this reduction be too great when the hydroxylic H becomes attached to some other element than O, such as N in aniline. Then again the Lorentz-Lorenz expression does not give a true interpretation for the liquid state, being only applicable if it is assumed that the molecules move independently of one another. The deviation in the refractive index for a binary mixture also agrees very closely with the change in density, so that any actual variation in the refractive index tends to become obscured. Finally the use of arbitrary wavelengths introduces another source of error. It is clear, then, that the non-existence of a deviation in the molar refractivity does not conclusively prove that an electronic link is wrong.

(2) The Evidence for a Resonance Linkage.

(In the following discussion Sidgwick's original idea of a co-ordinate linkage has been used, simply because of ease of representation, but a resonance state should be understood.)

If the idea of a link be provisionally accepted, then three structures only can be formulated for the compound between aniline and *o*-chlorophenol:—

- I. A link from the N of aniline to the phenolic H of *o*-chlorophenol.
- II. A link from the O of *o*-chlorophenol to a H of the $-\text{NH}_2$ group of aniline.
- III. A link from the Cl of *o*-chlorophenol to a H of the $-\text{NH}_2$ group of aniline.

Structure I., and probably also structure III., would require the chelate ring of *o*-chlorophenol to be opened.

The existence of ammonium salts shows the strong donating power of N; and as NH_3 is unassociated, it proves that H attached to N is a very weak acceptor. This makes structures II. and III. unlikely. Moreover, if the chelate structure is opened, the hydroxyl H is much more likely to accept from N, as in I., than Cl donate to a H of the $-\text{NH}_2$ group, as in III. The most probable structure is therefore I.

Now the heat change on mixing two organic liquids gives a fair indication of the occurrence and extent of compound formation. This property was therefore used in deciding between these three structures, the observed temperature changes being taken as roughly proportional to the heat changes. The following results were obtained:—

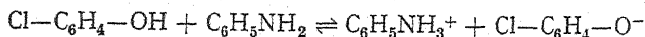
(a) aniline + <i>o</i> -chlorophenol	. . .	+ 12.3°
(b) aniline + chlorobenzene	. . .	— 4.0°
(c) aniline + anisole	. . .	— 0.5°
(d) dimethylaniline + <i>o</i> -chlorophenol		+ 6.0°

The large heat evolution thus completely vanishes when the hydroxyl hydrogen of *o*-chlorophenol is removed. The negative values for (b) and (c) merely indicate deassociation of the components on mixing. Structures II. and III. are thus opposed, and so structure I. is almost certainly the correct representation. A definite resonance linkage thus provides the simplest explanation of the reaction.

The extent of compound formation is approximately halved when aniline is replaced by dimethylaniline, but there is possibly a certain amount of steric hindrance in this case, the methyl groups preventing the approach of the hydroxyl group to the nitrogen atom.

(3) The Evidence for an Ionic Linkage.

The following equation would express the reaction if ions were formed:—



and it will be seen that the reaction is merely an extreme case of the sharing of H with the two atoms.

Ionic linkages were used by Howell and Robinson⁶ to explain their conductivity results for phenol—*o*-aniline and phenol—*p*-toluidine mixtures. They found it necessary to assume that the manner of ionisation was different at different concentrations; and their equations involved the unlikely assumption that a hydrogen ion from aniline would readily attach itself to $\text{C}_6\text{H}_5\text{OH}_2^+$. Undoubtedly phenolic compounds can ionise, but the conductivity of polar organic liquids is so influenced by disturbing factors that interpretations are somewhat arbitrary.

It will be seen that the ionic formula for the aniline—*o*-chlorophenol compound is very similar to aniline hydrochloride: $\text{C}_6\text{H}_5\text{NH}_3^+ \text{Cl}^-$. Now, although NH_4Cl is completely ionised in solution, it is considered that NH_4OH exists largely as unionised molecules containing a resonance linkage, *viz.* $\text{H}_3\text{N} \equiv \text{N} \text{H} \text{O} - \text{H}$; and since both water and phenolic compounds exist in equilibrium with their ions, this view further supports the possibility of a resonance linkage.

⁶ J.C.S., 1933, 1032.

It seems, therefore, that the negative results obtained by Smyth and others for the change of molar refraction of associated substances, and by the author for compound formation, cast doubt not so much on the existence of a link, as on the formula by which the molar refraction is calculated. This does not mean, however, that dipole association never occurs; but it is probably of a much weaker nature than the resonance linkage.

The Stability of Chelation in Orthophenols.

The usual association tests have revealed that many *ortho*-phenols, unlike the *meta* and *para* compounds, are unassociated. Kremann and Rodinis⁷ have shown that aniline gives compounds with *meta* and *para* nitrophenols, but not with the *ortho* compound, and this has recently been attributed to the stability of the internal resonance link. The compound formed with *o*-chlorophenol, then, must mean that in this substance the link is very much weaker, and more easily broken. This is only to be expected; partly because a link with Cl is weaker than with O, and partly because *o*-nitrophenol has a 6-membered ring, whilst *o*-chlorophenol has the less stable 5-membered ring.

Glass, Madgin and Hunter⁸ recently determined the heats of reaction for pyridine—*o*-chlorophenol by calculation from the freezing-points of dilute mixtures dissolved in inert solvents, and obtained a value of $q = -6800$ cal. (Bramley,⁹ $q = -4519$ cal.). By working in solution the components were completely deassociated; hence the high value. Then, for the system *p*-toluidine—*o*-cresol, containing no chelate ring, they obtained a value $q = -6000$ cal. It thus appears that a *greater quantity* of heat is evolved when the chelate ring is broken, and so they suggest that perhaps there is no chelation in *o*-chlorophenol. These two pairs of substances, however, are not strictly comparable, as the unchelated component is not the same for both mixtures. Further work is necessary to enable a decision to be reached on this point; and a redetermination of the heats of reaction between aniline and *o*-chlorophenol, in inert solvents, is at present being carried out.

Summary.

1. Refractive indices of anhydrous aniline—*o*-chlorophenol mixtures have been measured.
2. The extent of departure of the molar refractivities from the mixture law has been found to be no greater than the experimental error; but Smyth's argument for dipole association has been criticised, and a resonance linkage for the compound has been proposed.
3. The stability of chelation in *o*-chlorophenol has been discussed.

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⁷ *Monats.*, 1906, **27**, 136.

⁸ *J.C.S.*, 1933, 193 and 1431; 1934, 260.

⁹ *Ibid.*, 1916, **109**, 434, 496.

HEATS OF REACTION AND SPECIFIC HEATS OF ANILINE—*o*-CHLOROPHENOL MIXTURES: AND A TEST OF MACLEOD'S VISCOSITY EQUATION.

By C. D. ELLYETT.

Received 28th May, 1937.

Densities, viscosities, and freezing-points of aniline—*o*-chlorophenol mixtures have been determined by Bramley,¹ the values showing the existence of an equimolecular compound.

An expression for the viscosity of a binary mixture which has undergone volume change and compound formation has recently been derived by Macleod;² and, using Bramley's experimental values, he has obtained the percentage compound formation for the equimolecular mixture at various temperatures.

The object of the present work was a determination of the specific heats and heats of reaction of this system at several temperatures, enabling the equilibrium constants, and hence percentages of compound formation, to be determined independently of Macleod's viscosity equation.

Experimental Section.

(a) **Heats of Reaction.**—Macleod and Wilson,³ who recently measured the heats of reaction of ether-chloroform mixtures, suspended their reaction apparatus in a weighed quantity of water in a Dewar flask. The water brought the apparatus to a steady initial temperature, and reduced the magnitude of the temperature rise in the mixture, thus reducing uncertainties due to thermal deassociation of the compound and the components. This principle was adopted, but considerable changes in design were necessary to give accurate results at higher temperatures.

The thin copper reaction vessel and glass pipette were similar to Macleod and Wilson's, except that the vessel and stirrer were thickly plated with gold to overcome reaction with the organic liquids. A stirrer, consisting of three flat copper rings one above the other, was run at 200 oscillations per minute, and travelled up and down the stem of the Beckmann thermometer, keeping it in continual vibration. This overcame any tendency of the mercury to stick when falling temperatures were being recorded.

The aniline and *o*-chlorophenol, being hygroscopic, were weighed in double glass-tap pipettes without coming into contact with moisture; and xylene was used as the bath for the reaction vessel. The xylene was kept at a nearly constant temperature by an immersed heating coil, and temperature readings were taken every half-minute for four minutes. The liquid in the pipette was then forced over into the reaction vessel by dry compressed air, and the maximum temperature noted, together with the time taken for it to be attained. Readings were then taken every half-minute for another four minutes, and the true temperature rise calculated.

¹ *J.C.S.*, 1916, 109, 11, 434, 496.

² *Trans. Faraday Soc.*, 1934, 30, 482.

³ *Ibid.*, 1935, 31, 596.

A small correction was applied so as to bring the heat of reaction results to an exact temperature. The mean of the temperature on mixing and the maximum temperature was considered as the actual temperature at which the mixing took place, and in general this was not at an exact value. Therefore when all the results had been obtained a graph was constructed showing the fall in the heat of reaction per degree rise, for all molecular percentages. This gave the number of calories required to convert the heat of reaction from the experimental temperature to the desired even value.

(b) **Specific Heats.**—The material was placed in a thin copper cylinder, 12 cms. long and 3 cms. in diameter. This was coated with a layer of pure tin, and a ring of cork held it well down inside a heavy copper cylinder, which formed the inner surface of a closed cylindrical jacket. Water, after flowing through a 12-foot copper coil, immersed in a constant temperature bath, passed through the jacket. Two covers of sheet "bakelite" were screwed down over asbestos to the top of the jacket, so as completely to enclose the small cylinder.

A gold-plated ring stirrer rode up and down a Beckmann thermometer at 420 oscillations per minute, and caused a definite heating up of the liquid. The results were more reproducible at this speed, however, and provided the speed was steady, the temperature rise could be allowed for. Two very small platinum heating coils were fixed near the bottom of the liquid in the central cylinder. One coil passed into two thin glass tubes, where contact was made with the leads through mercury, and the other coil was wound on the outside of the tubes.

The same electrical circuit was used for both the specific heat and the heat of reaction apparatus. Constant current for the heating coils was controlled by variable resistances, the energy input being measured by means of standard ammeters and voltmeters. The hot water jacket was kept slightly below the required temperature, and the organic liquid itself kept at the exact temperature by one of the platinum coils in the liquid, the small rate of loss of heat being just counterbalanced by the energy input. The main heating circuit was then switched on for an exact time, and the temperature rise noted.

Purification of Materials.

Aniline.—Hopkins and Williams A. R. aniline was used. Small quantities were stood over purest anhydrous K_2CO_3 for several weeks, and then twice distilled in a dry all-glass apparatus. The purity and freedom from moisture were proved by refractive index determinations.

o-Chlorophenol.—A commercial product was twice distilled, then stood over pure anhydrous Na_2SO_4 , and finally redistilled, when practically the whole volume came over at a constant temperature.

Results.

Specific Heats.—Five or more concurrent determinations of the specific heat of each mixture were made, the results being reproducible to within 0.002 cal. The results for the pure components and the binary mixtures at 25°, 35°, and 78° C. are given in Table I. These results when plotted give smooth curves concave to the molecular percentage axis, the extent of departure from the additive value decreasing as the temperature is raised.

There are at least five superimposed effects which must be considered in explaining these curves.

1. A large heat evolution on mixing shows the formation of a chemical compound. The decomposition of this compound with rising temperature must therefore be attended by an absorption of heat, giving an abnormally large heat capacity.

2. Deassociation of either of the pure components with rising temperature also absorbs heat, again giving a positive deviation.

3. Compound formation, however, decreases the number of molecules, and hence the number of degrees of freedom. This should give a decreased heat capacity.

4. Dilution (on mixing) also causes deassociation. Hence an associated liquid may have a heat capacity in solution smaller than its heat capacity in the pure state.

5. Finally departure of internal pressure from the arithmetical mean, as evidenced by volume change on mixing, must affect the heat capacity.

By treating Bramley's density figures mathematically, Macleod

has shown that there is a small but definite contraction for aniline — *o*-chlorophenol, but the density curve is so nearly linear that the effect on the heat capacity can probably be ignored. In any case, Macleod⁴ states that the work done in overcoming the internal forces of a liquid is not greater than 1 per cent. of the total work done in raising the liquid 1° C. Now Table I. shows that there is a large positive deviation from additive values at all three temperatures. This can only mean that the effects due to 1 and 2 must override the effects

TABLE I.

Mol. Per Cent. <i>o</i> -Chlorophenol.	Specific Heat (Exptl.).	Additive Value.	Deviation.
Temperature, 25° C.			
0·00	0·496	(0·496)	0
17·05	·493	·479	+ 0·014
45·40	·483	·449	+ ·034
63·80	·466	·430	+ ·036
78·43	·446	·414	+ ·032
90·99	·420	·401	+ ·019
100·00	·392	(·392)	0
Temperature, 35° C.			
0·00	0·4994	(0·4994)	0
9·04	·499	·490	+ 0·009
27·77	·491	·470	+ ·021
40·76	·484	·456	+ ·028
56·82	·471	·440	+ ·031
68·21	·461	·428	+ ·033
88·18	·425	·407	+ ·018
100·00	·395	(·395)	0
Temperature, 78° C.			
0·00	0·5295	(0·5295)	0
10·10	·525	·518	+ 0·007
34·25	·506	·490	+ ·016
67·93	·469	·452	+ ·017
88·02	·437	·429	+ ·008
100·00	·415	(·415)	0

due to 3 and 4. Also it is known that aniline is only moderately associated at ordinary temperatures, and *o*-chlorophenol is unassociated, possessing instead an intra-molecular link; so it is unlikely that the deassociation factor will be large compared with the amount of compound decomposition.

This intra-molecular link, however, involves a specific effect. As will be shown in another paper, the formation of the compound necessitates the breaking of this link. Therefore the free *o*-chlorophenol molecules produced by decomposition of the compound with rising temperature must immediately reform the link, evolving heat. This change, however, takes place to exactly the same extent as the decomposition of the compound, and is not therefore an independent factor. Moreover,

⁴ *Trans. Faraday Soc.*, 1935, 31, 746.

the large heat evolution on mixing shows that its effect must be small compared with the energy evolution on forming the new link. The net result will thus be a slight decrease in the heat capacity, proportional to the decrease of combination with temperature.

It appears therefore as if the abnormally large heat capacity is due almost entirely to the absorption of heat caused by dissociation of the compound with rising temperature. These results lend support to the approximation made in the next section, that the amount of compound formation is proportional to the heat of reaction.

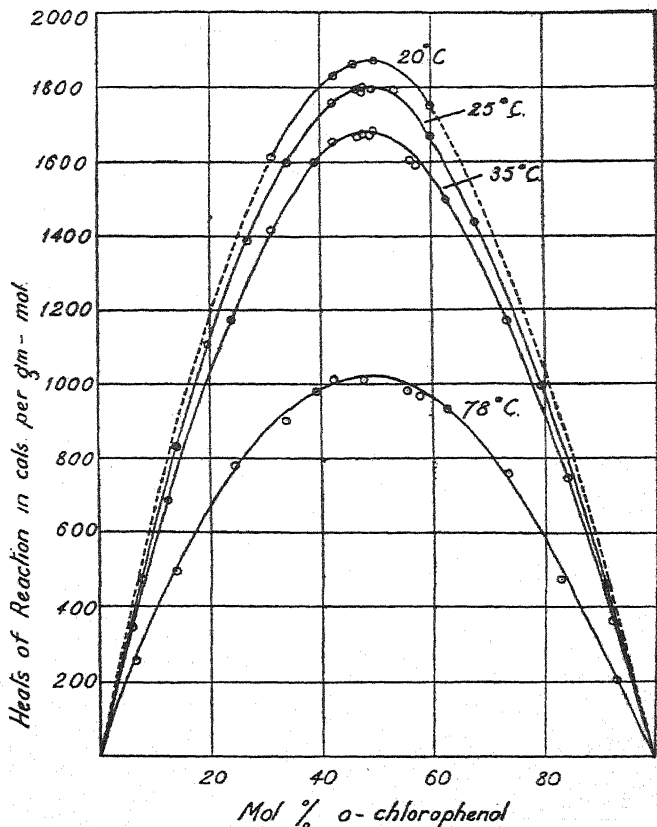


FIG. 1.

Bramley¹ determined the specific heat curves for *o*-chlorophenol with other substances, over a range 0°-20° C., obtaining very peculiar results exhibiting both maxima and minima; but the above discussion shows that average results over a twenty degree interval must give interpretations of very doubtful value. If the various mixtures were redetermined at definite temperatures, the specific heats would probably be found to lie on simple curves analogous to the aniline-*o*-chlorophenol mixtures.

Heats of Reaction, and Application of the Law of Mass Action.—The specific heat of the xylene surrounding the reaction vessel

TABLE II.

Mol. Per Cent. <i>o</i> -Chlorophenol.	Gram-cals. per gm. mol.	K.
Temperature, 20° C.		
31.55	1615	
42.59	1831	
45.62	1862	
49.74	1874	
59.65	1754	
Temperature, 25° C.		
7.60	474	0.00149
14.21	831	.00165
20.01	1117	.00167
27.10	1391	.00175
34.20	1603	.00178
42.03	1765	.00172
46.33	1807	.00164
47.42	1801	.00170
47.44	1792	.00166
49.39	1804	.00165
53.27	1795	.00149
59.65	1689	.00149
68.08	1447	.00136
77.43	1098	.00113
79.39	1000	.00112
90.99	466	.00054
90.99	467	.00048
Temperature, 35° C.		
5.95	347	0.00240
12.21	685	.00222
24.20	1185	.00250
31.35	1425	.00233
39.09	1612	.00220
42.41	1650	.00211
47.06	1676	.00212
47.79	1679	.00211
48.98	1679	.00209
49.68	1693	.00203
56.37	1617	.00203
57.25	1603	.00202
63.05	1508	.00183
73.53	1183	.00163
84.12	752	.00136
92.41	370	.00117
Temperature, 78° C.		
6.54	259	0.00764
13.73	497	.00772
24.67	776	.00739
33.95	891	.00789
39.37	972	.00692
42.65	1008	.00696
47.97	1005	.00725
55.71	972	.00689
57.68	962	.00679
62.69	921	.00636
73.47	756	.00593
83.24	467	.00705
92.98	199	.00740

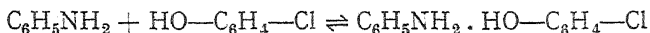
was first determined at 20°, 25°, 35°, and 78° C. Values for the heats of reaction were then obtained at these temperatures, the specific heats necessary in calculating the 20° results being obtained by extrapolation from the other specific heat curves. The results are given in Table II., and shown graphically in Fig. 1.

Two results were obtained at 25° C., using liquids which had been exposed to the atmosphere for five hours, equal quantities being exposed without stirring. The heat of reaction determined with nearly equimolecular mixtures of these liquids showed a decrease of 70 calories per gm. mol., and the specific heat of the mixture at 35° C. was raised 0.018 cal. These figures show clearly the magnitude of the errors introduced when moisture is not eliminated.

The freezing-point diagram for aniline — *o*-chlorophenol, determined by Bramley, shows that any liquid mixture lying between 35 and 64 mol. per cent. *o*-chlorophenol is in the supercooled state at 25° C. The heats of reaction, specific heats (and refractive indices, even with 24° of super-cooling) were uninfluenced by this state.

A close study of Fig. 1 showed that although the maximum heat of reaction occurred at approximately 50 mol. per cent., the curves were not completely symmetrical. At all temperatures the *o*-chlorophenol-rich side was steeper than the aniline-rich side, due probably to de-association of the aniline when added to a relatively large bulk of *o*-chlorophenol.

This, and similar effects, however, are small compared with the heat of reaction. If they are neglected, then the Law of Mass Action can be applied to the reaction



and an equilibrium constant obtained.

If A and B represent the number of gram-molecules of the two components in a mixture of volume V , and if X gm.-mols. of AB are present in the equilibrium mixture, then the equilibrium constant K is given by the expression:—

$$K = \frac{(A - X)(B - X)}{VX}$$

If X , the amount of compound formation, is proportional to H , the heat of reaction per gm.-mol., then $X = CH$, where C is a constant, so that

$$K = \frac{(A - CH)(B - CH)}{VCH}$$

On substituting two sets of values for A , B , V , and H , two equations are obtained, which can be solved for C and K . The calculation was simplified by making V have a constant value of 100 c.c., and the necessary densities were interpolated from Bramley's very full density results.

Bramley was the first to test this equation, using quinoline-*o*-chlorophenol mixtures at 0° C. only. He found that molecular dissociation prevented a trustworthy value of K being obtained. Macleod and Wilson,³ however, obtained fairly good constants with ether-chloroform mixtures, the components of which are non-associated. It was therefore necessary to see if the constants C and K for the present mixture were really constant, as otherwise the equation $X = CH$ could not be expected to give the true amount of compound formation.

Macleod⁴ has recently suggested, from a study of specific heat data, that a greater quantity of heat is associated with each degree of freedom at a higher temperature, and that therefore combination between two different molecules, with resulting loss of degrees of freedom, should produce a greater heat evolution the higher the temperature. If this were correct, it would mean that the constant C (referred to $V = 100$ c.c.) would have a steadily decreasing value with increasing temperature. The results calculated by Wilson⁵ for ether-chloroform showed that individual variations in the constant, obtained by using different molecular percentages, were far greater than any small decrease with increasing temperature. In the less ideal system aniline-*o*-chlorophenol a number of values of C were calculated for each temperature. The individual variations were again considerable, and the average value appeared to *increase* with temperature. The increase, however, was no greater than the individual variations, and as it was of doubtful significance, a mean value of 0.00032 was used in calculating K and X . These results therefore do not support Macleod's theory of increasing heat of reaction with temperature, but neither do they definitely disprove it. All that can be said is that if there is an increase it must be very small.

Values of K are given in Table II. It will be seen that the constants are reasonably good, except for *o*-chlorophenol-rich mixtures at 25° and 35° C. The calculated values for the percentages of combined molecules at equimolecular proportions should therefore be fairly close approxi-

⁵ Unpublished.

mations to the correct values. The results obtained were 57.42 per cent. at 25° C., 53.42 per cent. at 35° C., and 32.32 per cent. at 78° C.

The amount of combination near the boiling-point was also determined. For this purpose equimolecular quantities of the two pure liquids were brought to 166.8° C. by means of an oil bath, and were then

TABLE III.

	Macleod's Viscosity Formula.	Heats of Reaction.
20° C.	91.2 per cent.	59.0 per cent.
40° C.	51.7 "	50.5 "
60° C.	34.6 "	39.6 "
80° C.	26.0 "	31.4 "
150° C.	14.7 "	16.0 "

mixed by breaking an inner glass vessel. Several determinations were made, and the experiment was then repeated at 25° C.; whence, by proportion, the temperature rise at 166.8° C. was found to correspond to 14 per cent. combination. This result, of course, was very approximate, but it did show that there was about 12.16 per cent. combination at this temperature.

The values at the different temperatures were plotted, and percentages read off at the temperatures used by Macleod when calculating the combination from his viscosity formula. The two sets of independent values are compared in Table III.

For temperatures above 40° C., good agreement is obtained considering the accuracy possible with this type of work. Using Macleod's formula, the combination appears to rise very steeply to 91.2 per cent. at 20° C. His viscosity equation, however, is a function of the free space, which increases very rapidly with rising temperature near room temperature. The chance of error in the calculated viscosity is thus increased. Association changes also introduce uncertainties which will be more pronounced at low temperatures, and so an accurate value for the percentage combination from viscosity data is hardly to be expected. At these temperatures deassociation will also make the heat of reaction, and hence the percentage combination, lower than it should be. It can therefore be concluded that Macleod's viscosity formula closely represents a complex mixture of this type at high temperatures, but for mixtures near room temperature the values become uncertain.

Summary.

1. Heats of reaction and specific heats have been measured for aniline—*o*-chlorophenol mixtures at 25°, 35°, and 78° C.
2. The percentages of compound formation, calculated by means of the Law of Mass Action, have been compared with the values obtained by Macleod from his viscosity formula, agreement being obtained at higher temperatures. An account has been given of the disturbing factors at lower temperatures.
3. No support has been obtained for Macleod's theory of increasing heat of reaction with temperature.

In conclusion I should like to thank Dr. D. B. Macleod for suggesting this work, and for his constant interest and advice. I should also like to thank Professor C. C. Farr, F.R.S., for placing the facilities of the Physical Laboratory at my disposal, and for his kindly interest in this work.

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COLLISION, CO-ORDINATION, DIFFUSION AND REACTION VELOCITY IN CONDENSED SYSTEMS.

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I. Collision Number in a Dense System of Rigid Molecules.

It was demonstrated previously¹ that collisions of two particles (A and B) in a space densely populated with other particles (C, D, . . .) occur in *sets*. It was assumed that inter-set intervals increase with increasing density in the same measure as the sets become longer, and that the total number of collisions A-B per second, Z_{AB} , remains unchanged.

The author is indebted to Mr. M. J. Polissar (San Francisco) for directing his attention to the fact that the last conclusion is not exact. From considerations of the mean free path he concluded that Z_{AB} must *increase* with increasing concentration. The following reasoning will lead us to the same conclusion.

It was assumed¹ that the probability of finding A and B in collision is independent of the presence of other particles C, D, . . . in the same space, V. This assumption was derived by considering the paths covered by A and B in a sufficiently long time. If the particles C, D, . . . do not occupy fixed places, the paths of A and B must cover uniformly the whole space V, in presence of the other particles as well as in their absence. We concluded that the number of *crossings* of the two paths per second must be independent of the presence of other particles too.

This is, however, only true for two *independent* paths. In a densely packed medium each particle A is surrounded by a number of particles touching (or nearly touching) it. These form what we will call the "first co-ordination sphere" of A, with a radius about equal to the diameter a of A. This sphere is surrounded by a second one with a radius $\simeq 2a$, and so on. In a perfect lattice, the arrangement extends over thousands of concentric spheres; in liquids, the regularity is lost at a distance of a few molecular diameters from A. In the region around A where the arrangement in concentric spheres is recognisable, the probability of finding a second particle, B, at a certain distance r from A, $P(r)$, is a periodic function of r , with maxima corresponding to the radii of the successive co-ordination spheres and minima between them, whereas *in vacuo* $P(r)$ is a monotonous function of r , $P(r) = \text{const.} \times r^2$. This means that as soon as B reaches the region where the orderly arrangement of particles around A begins to prevail, its further movement is affected by the presence of A—and this long before an actual collision. The paths of A and B in a condensed system are therefore not independent paths in the sense in which they are such in a gas, *i.e.*, always but for actual collisions.

The existence of a periodicity of the above-discussed kind was first

¹ E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, 1936, **32**, 1381.

suggested by Keesom and de Smedt² and Zernicke and Prins³ as an explanation for the X-ray diffraction patterns of liquids. Debye and Mecke⁴ calculated the form of $P(r)$ for liquid mercury, and Kratky⁵ showed that this curve is best explained by a kind of hexagonal closest packing of the Hg molecules. Models illustrating the periodicity were constructed by Debye and Mecke,⁴ and, more recently, by Morrell and Hildebrand.^{5a} The same ideas are found in most of the modern theories of the liquid state.⁶

The curves of Debye and Mecke show the first maximum of $P(r)$ to be about five times its average value. If the probability of finding B in the "first co-ordination sphere" of A is five times larger than it would be in a gas, then the number of collisions Z_{AB} must be increased in the same proportion as well. With the packing density increasing further and further, Z_{AB} must tend to infinity, because the total number of particles in a given volume remains finite, even in the limiting case of solidly packed medium (whereas the mean free path becomes zero).

The mechanical model used¹ showed the occurrence of collision-sets, but revealed no change in Z_{AB} with increasing concentration. This negative result may be due to two causes (a) the length of the collision sets may already begin to grow when Z_{AB} is still nearly independent of concentration; (b) the "temperature" of the model may decrease with increasing concentration. (The balls on the plate were agitated by shaking the model. It is possible that at a given shaking velocity, the mean energy acquired by a ball decreases with increased number of balls on the plate). A decrease in velocity may thus counteract the influence of the decreasing mean free path on Z_{AB} .

These remarks do not affect the main results of our model experiments: the proof of the existence of collision sets. We can now say that by going over from a pair of rigid particles A and B in a diluted gas to the same particles in a closely packed medium, *two* changes take place:

(a) The total number of collisions Z_{AB} increases by a factor which is of the order of 5 at the densities corresponding to those of liquid mercury.

(b) The time-distribution of collisions A-B undergoes a change, characterised by the occurrence of *sets*, interrupted by longer *inter-set intervals*.

II. Collisions and Co-ordinations.

In Part I., the particles were supposed to be rigid. The existence of real condensed systems is, however, due to the non-rigidity of molecules. The time a molecule B remains in the first co-ordination sphere of A is not a "collision-set," i.e., a number of collisions with free paths between them, but rather a period of uninterrupted interaction.

Under these conditions, the notion of the "collision frequency," Z_{coll} , loses much of its meaning, and a new notion, that of the *co-ordination frequency* $Z_{\text{co-ord}}$ can be introduced, showing how often B comes into the first co-ordination sphere of A. Co-ordinations have a certain average duration θ and are composed of $\theta\nu$ vibrations of the system A-B. We

² W. H. Keesom and J. de Smedt, *Proc. Amsterdam Acad.*, 1927, 25, 118.

³ F. Zernicke and J. A. Prins, *Z. Physik*, 1927, 41, 184.

⁴ P. Debye and H. Mecke, *Physik. Z.*, 1930, 31, 797; 1932, 33, 593.

⁵ O. Kratky, *ibid.*, 1933, 34, 482.

^{5a} W. E. Morrell and J. H. Hildebrand, *J. Chem. Physics*, 1936, 4, 224.

⁶ See for instance the 1936 Discussion, *Trans. Faraday Soc.*, 1937, 33, No. 1.

assume at first that A and B are identical with the molecules of the "solvent" (a generalisation will be discussed in Part IV.). The co-ordinations of A and B are brought about by diffusion. We suppose that diffusion occurs by single displacements of the length a (shortest distance between two lattice points). The diffusion-coefficient D is given by the number m of displacements per second.

$$D = ma^2/2 \text{ (sq. cm. per sec.)} \quad (1)$$

(derived from $\bar{\Delta}^2 = 2D$ and $\bar{\Delta}^2 = ma^2$, where $\bar{\Delta}^2$ is the mean square displacement per sec.). The mean time between two displacements is

$$1/m = a^2/2D \quad (2)$$

The average duration of a co-ordination is

$$\theta = a^2\gamma/4D \quad (3)$$

The factor $1/2$ is due to the possibility of the co-ordination being terminated by a displacement of either A or B; the factor $\gamma (> 1)$ to the possibility of a displacement not affecting the co-ordination. For the hexagonal closest packing, for instance, only 6 out of 11 displacements which are allowed to B when in co-ordination with A interrupt this co-ordination ($\gamma = 11/6$).

The aggregate time A and B are in co-ordination in 1 sec. is equal to the probability of finding B in one of the lattice points nearest to A:

$$\Theta = n/N_0 \quad (4)$$

(N_0 = total number of lattice points, n = co-ordination number of the lattice, $n = 6$ to 12). The co-ordination frequency is therefore

$$Z_{\text{co-or}} = \Theta/\theta = 4nD/N_0 a^2\gamma \quad (5)$$

For two particles in 1 c.c. of a liquid with a mol volume 60 c.c. and $D = 10^{-5}$ sq. cm./sec., we obtain, for instance, with $n = 10$, $a = 3\text{\AA}$ and $\gamma = 2$

$$Z_{\text{co-or}} = 2 \times 10^{-11} \text{ per sec.}$$

and for two particles in 1 c.c. of a solid with the same parameters, but $D = 10^{-12}$

$$Z_{\text{co-or}} = 2 \times 10^{-13} \text{ per sec.}$$

The collision frequencies in gases are of the order of 10^{10} at 1 atm., or 6×10^{10} at 2 molecules per c.c. $Z_{\text{co-or}}$ in an average liquid is thus ~ 30 times smaller than Z_{coll} in a corresponding gas.

The average duration of a co-ordination is

$$\begin{aligned} \theta &= 10^{-10} \text{ sec. } (D = 10^{-5}) \\ \theta &= 10^{-3} \text{ sec. } (D = 10^{-12}) \end{aligned}$$

The frequency ν is roughly equal to Debye's "limiting frequency" of the medium. Its value is $\sim 5 \times 10^{12}$. The number of vibrations during a co-ordination A-B is therefore from 500 ($D = 10^{-5}$) to 5×10^9 ($D = 10^{-12}$).

If we consider each vibration A-B during their co-ordination as an equivalent of a "collision," we may define a "collision number" in condensed systems.

$$Z_{\text{coll}} = n/N_0 \simeq 5 \times 10^{-9} \quad (6)$$

This is roughly twenty times the average collision-number in gases. The difference is due to the close packing; it is the same effect as was discussed in Part I. for rigid molecules. Z_{coll} depends on the properties

of the whole "solution" rather than on those of the particles A and B; n and N_0 are lattice constants, and the frequency ν may be imposed by the solvent even upon solute molecules which are different in mass or composition from the molecules of the solvent. The dependence of (6) on temperature is also very different from that of Z_{coll} in gases.

III. Reaction Velocity in Condensed Systems.

We now assume that A and B are capable of interaction (chemical reaction, quenching of fluorescence, sensitisation, etc.), requiring an activation energy E_{act} . In a gas, E_{act} must be supplied by the reaction partners. In a condensed phase, it can be transferred from the medium during the whole co-ordination period. It is a kind of mono-molecular transformation, the whole of the liquid or solid playing the rôle of a molecule, and the reaction co-ordinate A-B that of the bond in which the energy E_{act} must be concentrated. The expression for the probability of a concentration of this kind, first derived by Polanyi and Wigner, must be multiplied by the probability of the activation coinciding with a co-ordination of the reacting pair AB.

If A and B can react, the mean duration of their co-ordination becomes

$$1/\theta = 1/\theta_{\text{diff}} + 1/\theta_{\text{react}} \quad (7)$$

where θ_{diff} is given by (3), and θ_{react} by Polanyi and Wigner's expression

$$1/\theta_{\text{react}} = \nu e^{-E_{\text{act}}/RT} \quad (8)$$

The co-ordination frequency is not affected by reaction, and the probability of finding A and B in co-ordination is, using (5), (7), (3) and (8):

$$\Theta = \theta Z_{\text{co-or}} = n/N_0 (1 + a^2 \nu e^{-E_{\text{act}}/RT} / 4D) \quad (9)$$

The reaction velocity constant is

$$c = \Theta / \theta_{\text{react}} = n \nu e^{-E_{\text{act}}/RT} \left(1 + \frac{a^2 \nu e^{-E_{\text{act}}/RT}}{4D} \right) \quad (10)$$

Two extreme cases may be considered:

$$e^{-E_{\text{act}}/RT} \gg 4D/a^2 \nu \gamma (= \nu \theta_{\text{diff}}) \quad (A)$$

$$e^{-E_{\text{act}}/RT} \ll 4D/a^2 \nu \gamma \quad (B)$$

Case (A)—small activation energy, and (or) slow diffusion—means that activation occurs practically during each co-ordination. The velocity constant is

$$c = 4nD/N_0 a^2 \gamma = Z_{\text{co-or}} \quad (10A)$$

In Case (B)—large activation energy, and (or) quick diffusion—activation occurs only once in many co-ordinations.⁷ The reaction velocity is

$$c = n \nu e^{-E_{\text{act}}/RT} / N_0 = Z_{\text{coll}} e^{-E_{\text{act}}/RT} \quad (10B)$$

where Z_{coll} is defined by (6).

For a solution, at 20° C., with $D = 10^{-5}$, $a = 3\text{Å}$, $\nu = 5 \times 10^{12}$ and $\gamma \sim 2$, case (A) can only occur if $E_{\text{act}} \ll 2\text{Kcal}$. Only very quick reactions can thus follow (10A) in liquids; reactions of excited molecules (quenching of fluorescence, etc.) may often (but not necessarily) belong to this group. All the other reactions in liquids must follow (10B), i.e., the usual formula for gaseous reaction, but with a non-exponential

⁷ Compare J. Weiss, *Naturwiss.*, 1935, 23, 64.

factor depending more on properties of the solvent than on those of the reacting solute, and affected by external factors—hydrostatic pressure, temperature, etc.—in the same measure as they change N_0 and ν .

In the case of a solid, most of the reactions will obey (10A) at not too high temperatures.

In case (A), the apparent activation energy is essentially that of the diffusion process. In case (B), it is the activation energy of the chemical reaction itself, and roughly equal to that of the gas reaction. In case (A), the velocity must depend on viscosity η , which affects D ; in case (B) only a much slighter effect of η may be expected, due to a possible influence of viscosity on ν .

The influence of D (and impliedly of η) on processes occurring by the first collision of two particles in solution was first discussed by Smoluchowski (coagulation velocity) and then by Wawilow (quenching of fluorescence). Wawilow's formula, $c = 4\pi Dr$ (r = radius of the action sphere of the excited molecule) corresponds to (10A); the difference in factors before $D(4n/N_0 a^2 \gamma$ instead of $4\pi r$) is a consequence of the lattice-conception used in derivation of (10).

Svešnikov⁸ extended the theory to *thermal* reaction. He suggested than an influence of viscosity on reaction velocity can only occur if the activation periods involved are of the "optical" order of magnitude (up to 10^{-7} sec.), instead of the usually assumed 10^{-12} to 10^{-13} sec. From Svešnikov's own formula for the velocity of reactions with "long-living" activations, $c = 4\pi Dr [1 - (1 - p)^n]$ (p = probability of reaction by one collision, n = number of collisions in what we called¹ a "collision set"), it follows, however, that c is only proportional to D for $p \simeq 1$, and becomes independent of D for $p \ll 1$ (because n is proportional to $1/D$). The same was shown above for "short living" activations. Assumption of long-living activated states does not help therefore to explain the influence of η on the rate of relatively slow reactions ($p \ll 1$), as suggested by Svešnikov. Perhaps association-effects discussed in Part IV. are responsible for these cases, rather than the viscosity itself.

IV. Influence of an Association or Dissociation Tendency.

The above developed theory cannot apply to molecules of a size very different from that of the solvent molecules. An application may, however, be tried for molecules which differ from the solvent by mass or composition, but whose size makes an isomorphic replacement of one molecule of the solvent by one molecule of the solute possible. In liquids, the limits allowed for such a substitution are probably much wider than in solid crystals.

Formulae (3), (5) and (6) can be used in this case, D meaning the coefficient of diffusion of the solute. If D_A and D_B are different $D_A + D_B$ must be substituted for $2D$.

The state of co-ordination A-B will in general differ from the states in which A and B are separated, by an energy $E_{\text{co-or}}$. In the case $E_{\text{co-or}} < 0$ (association tendency), θ and Θ are increased by the factor $e^{-E_{\text{co-or}}/RT}$; $Z_{\text{co-or}}$ remains unchanged, and $(E_{\text{co-or}} + E_{\text{act}})$ is to be substituted for E_{act} in formula (10) for the reaction velocity c . (This is exact for $e^{-E_{\text{co-or}}/RT} \ll n/N_0$, meaning that the association remains a "weak" one.)

⁸ B. I. Svešnikov, *C.r. Acad. Sci. U.S.S.R.*, 1936, **3**, 61.

The case $E_{\text{co-or}} > 0$ ("repulsion") is more complicated. Θ is again multiplied by $e^{-E_{\text{co-or}}/RT}$; but the influence of $E_{\text{co-or}}$ on the two factors of which Θ is composed, θ and $Z_{\text{co-or}}$, depends on the nature of the diffusion constant D . If D depends only on frequency with which "holes" appear in the neighbourhood of A and B (see Part V.) then a positive $E_{\text{co-or}}$ cannot cause a quicker separation of the pair; θ remains unchanged; $Z_{\text{co-or}}$ is diminished in the same proportion as Θ ; and c is decreased by the factor $e^{-E_{\text{co-or}}/RT}$ both in case (A) (c determined by $Z_{\text{co-or}}$) and (B) (c determined by Θ). If, however, the diffusion requires a genuine activation energy E_{diff} , then $E_{\text{co-or}}$ can be used to supply it, θ will be shortened by a factor $\leq e^{-E_{\text{act}}/RT}$ (not $e^{-E_{\text{co-or}}/RT}$), and $Z_{\text{co-or}}$ will be correspondingly less affected; c will be diminished by the factor $e^{-E_{\text{co-or}}/RT}$ only in case (B), where Θ is the determining factor, and will be less strongly affected in case (A).

This generalisation of the theory may be of interest, for instance, in the treatment of reactions in which dipole molecules or ions are involved.

V. Diffusion Velocity.

The simplest possibility of diffusion in lattices was first indicated by Frenkel.⁹ It consists in a "diffusion of holes," i.e., an exchange of particles between occupied and empty lattice points. It was thought at first that, if holes occur, the "missing" particles must be found somewhere in "wrong" positions in the lattice. Jost¹⁰ and Schottky¹¹ showed, however, that a certain number of points must be unoccupied in the thermal equilibrium. We arrived independently at the same conclusion in the following way:

Some time ago¹² we deduced a vapour pressure formula for the evaporation of a sorbate (e.g., water) from a zeolitic crystal:

$$\log_e p = -\frac{\lambda}{RT} + \log_e \frac{N}{N_0 - N} + \left\{ \begin{array}{l} \text{specific heat terms and} \\ \text{chemical constants.} \end{array} \right. \quad (11)$$

N_0 means the total number of lattice points available for sorption and N the number of points occupied by the sorbate. The same statistical considerations which lead to (11) apply, however, also to every constituent of an "ordinary" crystal; because each lattice particle can be considered as "sorbed" by the lattice. In other words, (11) determines also the "internal vapour pressure" of an ordinary crystal—an evaporation equilibrium which leaves holes in the body of the crystal.

In thermodynamical equilibrium, the "internal" pressure must be equal to the "external" one—which is described by a formula analogous to (11), but with a smaller λ and without the "saturation" term $\log[N/(N_0 - N)]$. We thus obtain, for the equilibrium concentration of holes, the relation

$$(N_0 - N)/N = e^{-\Delta\lambda/RT} \quad (12)$$

with the abbreviation $\Delta\lambda = \lambda_{\text{int}} - \lambda_{\text{ext}}$. In the case of a purely additive binding force λ_{int} is simply twice λ_{ext} , because twice as many bonds must be disrupted for the formation of a hole as for the evaporation of a molecule from the surface. (This consequence has already

⁹ J. Frenkel, *Z. Physik*, 1926, **35**, 652.

¹⁰ W. Jost, *J. Chem. Physics*, 1933, **1**, 466.

¹¹ W. Schottky, *Z. Physik. Chem., B*, 1935, **29**, 335.

¹² E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, 1936, **32**, 947.

been used by Eyring¹³ in applying Schottky's ideas to liquids, especially to the explanation of the Cailletet-Mathias' rule).

In the case of non-additive binding, λ_{int} will be $< 2\lambda_{\text{ext}}$. The binding energy of two Na atoms is, for instance, ~ 18 Kcal. per mol.; that of a Na atom in solid sodium only ~ 30 Kcal., although one Na-Na bond is disrupted in the first case and four such bonds in the second. We may thus anticipate that the formation of a hole in a Na crystal, involving the severing of 8 Na-Na bonds, requires much less than twice the ordinary evaporation energy. The same must be true—although to a smaller degree—also for liquids with a strong dipole interaction—e.g., water.

The diffusion coefficient D is usually represented—as first suggested by Braune¹⁴—by

$$D = Ae^{-U/RT} \quad (13)$$

The activation energy of diffusion, U , is, according to the theory of "holes," mainly the energy of formation of holes, to which probably a relatively small real activation energy—that necessary for the transition from an occupied to an empty place,—must be added (see Jost).¹⁵ U in (13) must therefore be roughly equal to the evaporation energy for non-polar molecular lattices, considerably less than that for dipole systems, and still less for atomic lattices (metals).

No data are available for the diffusion of solid or liquid gases (Ar, Kr, O₂, N₂, . . .) which would provide the best examples of the first case; nor are there sufficient data for the diffusion of molecules of the kind of CCl₄, CBr₄, etc. The diffusion velocity of H₂O₂ into H₂O, which has been investigated by Stern,¹⁶ gives an activation energy $U \sim 5$ Kcal, i.e., roughly half of the evaporation energy of H₂O, which is in accordance with expectation. For Cu, Ag, Au, Pd, Pt, Jost¹⁷ calculated U -values of ~ 30 Kcal., which is of the order of 30 per cent. of their evaporation energies.

The factor A in (13) can be calculated in the same way as used in Part II. for the calculation of the co-ordination frequency; only we have now to consider the co-ordinations of a particle A with holes H . The probability of a co-ordination of A with any one of the $N_0 - N$ holes is

$$\Theta_H = n(N_0 - N)/N_0 \quad (14)$$

The number of displacements which result from these co-ordinations is

$$m = n(N_0 - N)ve^{-E_{\text{diff}}/RT}/N_0 \quad (15)$$

Together with (1), (15) gives

$$D = a^2n(N_0 - N)ve^{-E_{\text{diff}}/RT}/2N_0 \quad (16)$$

Since $N \simeq N_0$, we may introduce (12) into (16) and obtain

$$D = \frac{1}{2}a^2nve^{-(E_{\text{diff}} + \Delta\lambda)/RT} \text{ cm.}^2/\text{sec.} \quad (17)$$

This expression can be introduced into all the formulæ in Parts II., III., and IV. where the diffusion coefficient D occurs.

The non-exponential factor in (13) is thus

$$A = \frac{1}{2}a^2nv \text{ cm.}^2/\text{sec.} \quad (18)$$

¹³ H. Eyring, *J. Chem. Physics*, 1936, 4, 283.

¹⁴ H. Braune, *Z. physik. Chem.*, 1924, 110, 147.

¹⁵ W. Jost and G. Nehlep, *ibid.*, B, 1936, 32, 1.

¹⁶ K. G. Stern, *Ber.*, 1933, 66, 547.

¹⁷ W. Jost, *Z. physik. Chem.*, B, 1931, 16, 123; 1933, 21, 158.

For Ag, for instance, with $a = 2.8 \times 10^{-8}$, $\nu = 4 \times 10^{12}$ and $n = 8$, we obtain $A = 0.013$, which is not very different from the value found experimentally (0.002 for the diffusion of Au into Ag according to Jost). The theory gives thus the right order of magnitude both for the exponent and the non-exponential factor in the diffusion formula.

Formula (17) is primarily for self-diffusion. It may also apply for the diffusion of particles which are not too different from those of the solvent, especially in size. Two kinds of molecules of roughly the same size and the same kind of interaction with the medium—e.g., different ions of the same charge—will thus diffuse with but slightly different velocities. (In a gaseous medium, these velocities would be inversely proportional to $\sqrt{\mu} = \sqrt{M_{\text{Msolv}}/(M + M_{\text{Msolv}})}$.)

DIFFUSION INTO LIQUID MERCURY.

	$\sqrt{\mu}$.	D cm. ² /day.		$\sqrt{\mu}$.	D cm. ² /day.
Ca .	5.8	0.54	Li .	2.6	0.66
Sr .	7.8	0.47	Na .	4.5 _s	0.64
Ba .	9.0	0.52	K .	5.7	0.53
Sn .	8.65	1.53	Rh .	7.8	0.46
Pb .	9.8 _s	1.50	Cs .	9.9 _s	0.45

The examples shown in the table are in agreement with this anticipation. Other examples of the same kind are found in a paper by Seith.¹⁸

Differences in D for Sn and Pb on the one hand and the alkaline metals on the other hand, shown by

the above table, may be due to solubility effects of the following kind:

The generalisation discussed in Part IV. may be applied also to the diffusion formula. The dissolved particle A may have the tendency either to associate itself with a hole, or to repel it (i.e., to associate itself with the molecules of the solvent). The co-ordination energy $A \cdot H$ we designate ΔU_{solv} because of its relation with the solvation energy. The greater the solvation energy, the smaller the chance of finding a hole in the first co-ordination sphere of the solute. *Positive* ΔU_{solv} will always tend to make diffusion slower, by a factor $e^{-\Delta U_{\text{solv}}/RT}$; the influence of *negative* values of ΔU_{solv} will depend on the existence of a "true" activation energy E_{diff} (cf., Part IV.). If $E_{\text{diff}} \neq 0$, the diffusion coefficient will be increased by a factor $\leq e^{E_{\text{diff}}/RT}$ (not, however, $e^{-\Delta U_{\text{solv}}/RT}$).

Summary.

1. In densely populated systems of *rigid particles*, the collision frequency of two particles A and B is higher than *in vacuo*, by a factor which can be estimated from the X-ray diffraction patterns, on the basis of the theories of Zernicke and Prins, and Debye and Menke.

2. In *real* condensed systems (consisting of non-rigid molecules) the notion of *co-ordination frequency*, $Z_{\text{co-or}}$, can usefully be introduced instead of the collision-frequency Z_{coll} . Each co-ordination consists of a certain number of vibrations of the co-ordinated particles.

3. Formulae for $Z_{\text{co-or}}$ and the bimolecular reaction velocity c in condensed systems can be derived in terms of the diffusion coefficient. Two extreme cases must be distinguished. In that of slow diffusion (or low activation), c is equal to $Z_{\text{co-or}}$; it depends on D , and thus on viscosity, etc.

4. In the case of quick diffusion (or high activation) c is given by the same formula as in the usual collision theory, but the non-exponential

¹⁸ W. Seith, *Z. Elektrochem.*, 1935, 41, 872.

factor has a different meaning and depends on the properties of the solvent more than on those of the reacting solute molecules.

5. The empirical diffusion coefficient D can be replaced in the above reaction velocity formulæ by an expression derived from the notion of "lattice holes."

My heartiest thanks are due to Professor F. G. Donnan, F.R.S., for continuous hospitality in his laboratory.

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THE MOLECULAR STRUCTURES OF IRON NITROSOCARBONYL $\text{Fe}(\text{NO})_2(\text{CO})_2$ AND COBALT NITROSOCARBONYL $\text{Co}(\text{NO})(\text{CO})_3$.

BY L. O. BROCKWAY AND J. STUART ANDERSON.

Received 9th June, 1937.

The molecular structures of iron nitrosocarbonyl $\text{Fe}(\text{NO})_2(\text{CO})_2$ and cobalt nitrosocarbonyl $\text{Co}(\text{NO})(\text{CO})_3$ are of particular interest in their relation to that of nickel carbonyl $\text{Ni}(\text{CO})_4$. Reiff¹ pointed out that in $\text{Co}(\text{NO})(\text{CO})_3$ the deficiency of one electron on the cobalt atom as compared with nickel is made up by the one electron which nitrogen has more than carbon; the nitrogen atom contributes three electrons to the shell around the central atom and the cobalt compound, which is observed to be diamagnetic, presumably has the electronic structure of $\text{Ni}(\text{CO})_4$. Hieber and Anderson² called attention to the similar properties of $\text{Fe}(\text{NO})_2(\text{CO})_2$, $\text{Co}(\text{NO})(\text{CO})_3$, and $\text{Ni}(\text{CO})_4$ and applied the name "pseudo-nickel carbonyl" to the first two of these substances. They suggested that the nitroso group is linked to the central atom by a double electron-pair bond with a double bond between nitrogen and oxygen while the carbonyl group is attached by a single bond with a triple bond between carbon and oxygen. Sidgwick and Bailey³ discussed the probable structures of these compounds in some detail and maintained that the nitroso linking is the same as that of the carbonyl group. The electron diffraction investigation of the structure of $\text{Ni}(\text{CO})_4$ ⁴ showed that this molecule is tetrahedral and that the bond structure must involve resonance between $\text{Ni}:\text{C}::\text{O}:$ and $\text{Ni}::\text{C}::\text{O}:$ to account for the observed distances.

The present electron diffraction investigation of the nitroso compounds was undertaken in order that their bond distances might be used in interpreting the bond structures.

¹ F. Reiff, *Z. anorg. Chem.*, 1931, **202**, 375.

² W. Hieber and J. S. Anderson, *ibid.*, 1932, **208**, 238; 1933, **211**, 132.

³ N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc., A*, 1934, **144**, 521.

⁴ L. O. Brockway and P. C. Cross, *J. Chem. Physics*, 1935, **3**, 828.

Preparation and Purification of Materials.

Cobalt nitrosocarbonyl $\text{Co}(\text{NO})(\text{CO})_3$ was prepared by a variant of the method described by Blanchard, Rafter and Adams.⁵ A suspension of cobaltous cyanide in sodium hydroxide was shaken in carbon monoxide until absorption was complete. The suspension was acidified and treated with nitric oxide; absorption took place, and cobalt nitrosocarbonyl was formed. Contrary to the statement of Blanchard, Rafter and Adams, no formation of cobalt nitrosocarbonyl was observed in alkaline solutions. The material was dried by distillation through phosphorus pentoxide, and was fractionated in vacuum to a constant vapour pressure and constant melting point. The sample of material used for electron diffraction measurements was one that had been employed for measurements of physical properties.⁶

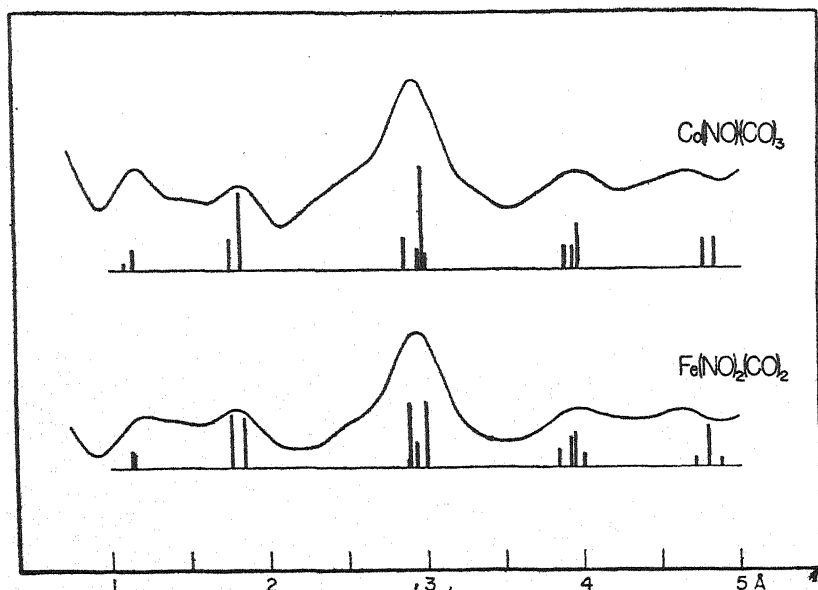


FIG. 1.—Curves showing the observed radial distribution of scattering matter in $\text{Co}(\text{NO})(\text{CO})_3$ and $\text{Fe}(\text{NO})_2(\text{CO})_2$. The vertical lines mark the observed interatomic distances and show the relative scattering power associated with each.

Iron nitrosocarbonyl $\text{Fe}(\text{NO})_2(\text{CO})_2$ was prepared by a method not hitherto described. Nitric oxide was circulated over iron tetracarbonyl, $\text{Fe}_3(\text{CO})_{12}$ at 85° , and condensable products were frozen out in a carbon dioxide-alcohol bath. The resulting mixture of iron nitrosocarbonyl and pentacarbonyl was separated by conversion of the latter to the mercury salt of iron carbonyl hydride, $\text{Fe}(\text{CO})_4\text{Hg}$. The iron nitrosocarbonyl was finally fractionally distilled in vacuum until the constant melting point 18.4° was attained. The details of this preparative method, which is of interest in connection with the constitution of iron tetracarbonyl, will be discussed in a separate publication.

Electron diffraction photographs of these substances were taken by the procedure which has previously been described.⁷ The samples were heated to about 40°C . and photographed at an electron wave-length of

⁵ Blanchard, Rafter and Adams, *J.A.C.S.*, 1934, **56**, 16.

⁶ J. Stuart Anderson, *J. Chem. Soc.*, 1936, 1283.

⁷ L. O. Brockway, *Rev. Modern Physics*, 1936, **8**, 231.

0.0611 Å. and a camera distance of 10.85 cm. The photographs of each substance show eight rings of which the second, third, and fifth are strongest, while the fourth appears as a subsidiary maximum to the third. This characteristic qualitative appearance of the pattern is shown by the photographs of both the iron and the cobalt compounds as well as by the earlier photographs of $\text{Ni}(\text{CO})_4$.⁴

The radial distribution functions (Fig. 1) were calculated from the measured values of $s_0 \left(= \frac{4\pi \sin \theta/2}{\lambda} \right)$ and the visually estimated intensities given in Tables I. and II. In the curve for $\text{Fe}(\text{NO})_2(\text{CO})_2$ peaks are observed at the distances 2.94 Å., 1.79 Å., 1.25 Å., and 3.9-4.0 Å. If we consider only models in which the two nitrogen and the two carbon atoms are bonded to the iron atom, the peak at 2.94 Å., which is strongest and most

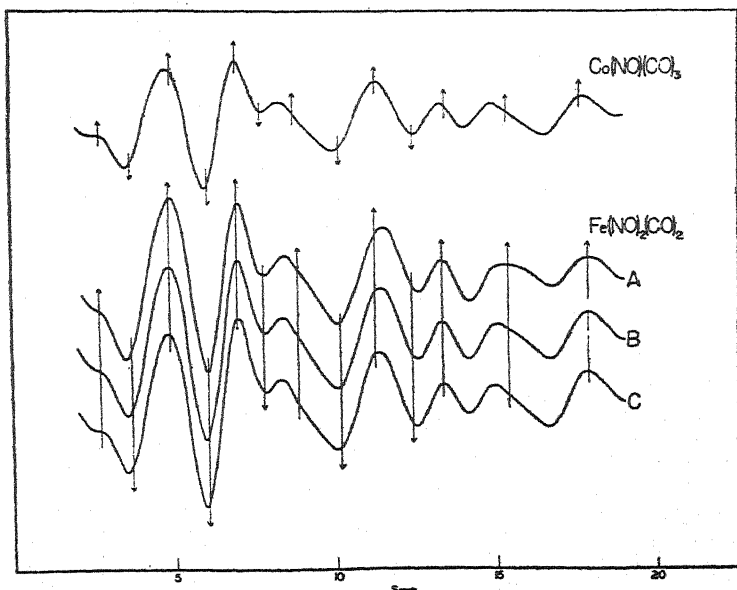


FIG. 2.—Theoretical intensity of electron scattering by various models of $\text{Co}(\text{NO})(\text{CO})_3$ and $\text{Fe}(\text{NO})_2(\text{CO})_2$. The arrows mark the positions of the maxima and minima observed on the photographs.

reliable, corresponds to the average of the Fe—O distances. The peak at 1.79 Å. represents the combination of the Fe—C and Fe—N distances.

In fixing the interatomic distances in the molecular models for which the theoretical intensity of electron scattering by $\text{Fe}(\text{NO})_2(\text{CO})_2$ was calculated, it was assumed that the Fe—C—O group has the same structure as Ni—C—O in $\text{Ni}(\text{CO})_4$. This makes C—O = 1.15 Å. and Fe—C = 1.84 Å., the latter being 0.02 Å. larger than the nickel-carbon distance in accordance with the larger size of the iron atom. The sum corresponding to Fe—O is 2.99 Å. The occurrence of the strong peak at 2.94 Å. in the radial distribution curve then requires that the length of the Fe—N—O group be close to 2.89 Å. Three models fulfilling these conditions and whose intensity curves are shown in Fig. 2 were calculated with the following iron-nitrogen and nitrogen-oxygen distances: (A) Fe—N = 1.71 Å., N—O = 1.18 Å.; (B) Fe—N = 1.75 Å., N—O = 1.14 Å.; (C) Fe—N = 1.78 Å., N—O = 1.10 Å. The four groups attached to the central atom are located in the tetrahedral directions.

Each of the curves reproduces very well the qualitative appearance of

the photographs except where the first ring is represented by a hump not completely resolved from the central image. Curve A is a little less satisfactory than B or C because its seventh ring is broad and rounded whereas the seventh ring in the photographs is about as sharp and well-defined as the sixth. In Table I. the quantitative comparisons of Models B and C with the photographs lead to the final values: Fe—N = 1.77 ± 0.02 Å., Fe—O = 2.89 ± 0.03 Å.; Fe—C = 1.84 ± 0.02 Å., and Fe—O = 2.99 ± 0.03 Å. Although the N—O and C—O terms are relatively less important in the scattering, differences between the foregoing pairs of values give the reliable results: N—O = 1.12 ± 0.03 Å. and C—O = 1.15 ± 0.03 Å. All of the interatomic distances occurring in the molecule are shown in the radial distribution curve by the heavy vertical lines whose heights are proportional

TABLE I.—IRON NITROSCARBONYL.

Max.	Min.	I.	s_0 .	s^* .	s/s_0 .	s^\dagger .	s/s_0 .
1		4	2.69				
	2		3.66	3.49	(0.954)	3.52	(0.962)
2		10	4.87	4.86	0.998	4.79	0.984
	3		6.04	5.97	0.989	5.95	0.986
3		6	6.96	6.96	1.000	6.96	1.000
	4		7.76	7.82	1.007	7.83	1.009
4		2	8.84	8.35	(0.945)	8.31	(0.940)
	5		10.17	10.06	0.989	10.07	0.990
5		4	11.21	11.42	1.018	11.34	1.011
	6		12.36	12.54	1.015	12.51	1.013
6		1½	13.31	13.33	1.002	13.33	1.002
7		1	15.40	15.06	(0.979)	14.92	(0.969)
8		1	17.88	17.89	1.000	17.86	0.999
			Average		1.002		0.999
				Fe—O	2.996 Å.		2.987 Å.
				Fe—O	2.896		2.877
				Fe—N	1.754		1.778
				Fe—C	1.844		1.838

* Calculated for model with
Fe—C = 1.84 Å., Fe—O = 2.99 Å., Fe—N = 1.75 Å.,
Fe—O = 2.89.

† Calculated for model with
Fe—C = 1.84, Fe—O = 2.99 Å., Fe—N = 1.78, Fe—O = 1.10.

the fact that the atomic scattering factors which are approximately proportional to the atomic numbers, are very nearly the same for both molecules. The square models for $\text{Ni}(\text{CO})_4$ were eliminated by their failure to reproduce the fourth maximum observed on the photographs; and since the fourth maximum for $\text{Fe}(\text{NO})_2(\text{CO})_2$ is the same both in position and appearance as that for $\text{Ni}(\text{CO})_4$, the square configuration for the iron compound may also be excluded.

The single theoretical intensity curve for $\text{Co}(\text{NO})(\text{CO})_3$ shown in Fig. 2 corresponds to a model with Co—C = 1.83 Å., Co—O = 2.98 Å., Co—N = 1.77 Å., and Co—O = 2.87 Å. This curve is satisfactory both in the qualitative appearance of the pattern and also in the quantitative comparison with the observed maxima and minima as shown in Table II. The observed values are Co—C = 1.83 ± 0.02 Å.; Co—O = 2.97 ± 0.03 Å.; Co—N = 1.76 ± 0.02 Å. and Co—O = 2.86 ± 0.03 Å. These are supported by the radial distribution curve, in which the strong peak at 2.93 Å. is produced by the three Co—O terms at 2.97 Å. and one at 2.86 Å., the peak at 1.82 Å. is due to the Co—C and Co—N terms while the other interatomic distances make the contributions shown by the vertical lines in the figure. The C—O distance is 1.14 ± 0.03 Å. and N—O is 1.10 ± 0.04 Å. The latter is determined with

to the scattering powers associated with each distance. The two strongest scattering terms giving rise to the peak at 2.94 Å. correspond to the two Fe—O distances. The Fe—C and Fe—N terms combine to give an unresolved peak at 1.79 Å. in good agreement with the above values for these distances. A square configuration of the four bonds on the iron atom is regarded as very improbable in view of the close similarity of both the photographs and the intensity curves with those for $\text{Ni}(\text{CO})_4$. This similarity is due to

less certainty in this compound because the contribution to the scattering by the nitroso groups is only a third of that of the three carbonyl groups. For the reasons given above this molecule also is very probably tetrahedral.

Discussion.

The bond distances observed in $\text{Fe}(\text{NO})_2(\text{CO})_2$, $\text{Co}(\text{NO})(\text{CO})_3$, and $\text{Ni}(\text{CO})_4$ are collected in Table III. These distances may be compared with the appropriate sums of covalent radii.⁸ The single bond covalent radii for iron, cobalt, and nickel when no orbitals higher than $3d$, $4s$, and $4p$ are involved have values from 1.21 Å. to 1.25 Å., as determined from the sulphides and arsenides. Adding 0.77 Å. for the radius of carbon we see that the metal-carbon single bond distance in each of these compounds lies within 0.02 Å. of 2.00 Å. The observed metal-carbon distances are from 0.16 Å. to 0.18 Å. below this value. The metal-nitrogen distances also are found to be about 0.16 Å. less than the corresponding single bond distance, 1.93 Å.

The observed carbon-oxygen distances, 1.15 Å., lie close to the value observed in carbon monoxide and are to be compared with the double bond radius sum, 1.24 Å., and the triple bond radius sum, 1.11 Å. This comparison suggests a resonance between electronic structures having a double and a triple electron-pair bond, respectively, between carbon

TABLE II.—COBALT NITROSOCARBONYL.

Max.	Min.	I.	s_0	s^*	s/s_0
1		3	2.71	2.66	(0.982)
	2		3.67	3.48	(0.948)
2		5	4.92	4.76	(0.968)
	3		6.03	5.93	0.984
3		4	6.96	6.94	0.997
	4		7.70	7.78	1.010
4		2	8.74	8.29	(0.949)
	5		10.14	9.93	0.980
5		4	11.28	11.29	1.001
	6		12.41	12.47	1.005
6		2	13.43	13.27	0.989
7		1	15.38	14.91	(0.970)
8		2	17.65	17.76	1.006
Average					0.997
					Co—O 2.971 Å.
					Co—C 1.825
					Co—O 2.861
					Co—N 1.765

* Calculated for a model with

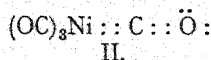
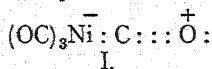
Co—C = 1.83 Å., Co—O = 2.98 Å.,
Co—N = 1.77 Å., Co—O = 2.87 Å.

TABLE III.

Bond Distances in $\text{Fe}(\text{NO})_2(\text{CO})_2$, $\text{Co}(\text{NO})(\text{CO})_3$, and $\text{Ni}(\text{CO})_4$.

	M—C	C—O	M—N	N—O
Fe	1.84 ± 0.02 Å.	1.15 ± 0.03 Å.	1.77 ± 0.02 Å.	1.12 ± 0.03 Å.
Co	1.83 ± 0.02 Å.	1.14 ± 0.03 Å.	1.76 ± 0.03 Å.	1.10 ± 0.04 Å.
Ni	1.82 ± 0.02 Å.	1.15 ± 0.03 Å.		

and oxygen, in which approximately equal contributions are made by the two structures.⁹ The following examples of electronic structures whose combined contributions to the normal state of the molecule would account for the observed distances were originally suggested for $\text{Ni}(\text{CO})_4$, but according to the observed distances in Table III., they apply as well to the "pseudo-nickel carbonyls."

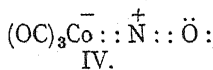
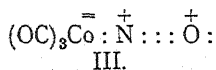


⁸ See L. Pauling and M. L. Huggins, *Z. Krist.*, 1934, 87, 228; also Sidgwick, *Covalent Link in Chemistry*, 1933, Cornell Univ. Press, pp. 85, 87.

⁹ For a discussion of the effect on bond distance of resonance between several electronic structures see L. Pauling, *Proc. Nat. Acad. Sci.*, 1932, 18, 293; L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Am. Chem. Soc.*, 1935, 57, 2705; L. Pauling and L. O. Brockway, *ibid.*, 1937, 59, August.

If equal contributions to the normal state were made by structures I. and II., the Ni—C bond distance would be shorter than the sum of the single bond radii by about 75 per cent. of the difference between the single and double bond distances; at the same time the C—O bond distance would lie closer to the triple bond value than to the double. The same possibility exists for the other three carbonyl groups, and, because there are nine available bond-forming orbitals on nickel, structures like II. can exist in two or more of the groups at the same time. In any event the distances observed in the four groups will be the same since equivalent sets of structures can be formulated with respect to each of the four. The same behaviour is expected of carbonyl groups in the iron and cobalt nitrosocarbonyls and this expectation is supported by the observed distances.

The N—O bonds are also observed to be shorter than the double bond distance, 1.18 Å. Although the accuracy of the determination of the N—O distances does not allow an estimate of the relative contributions of the double and triple-bonded structures, the shortening observed in the Fe—N and Co—N bonds indicates that the situation in the M—N—O groups is similar to that in the M—C—O groups. It is not likely that exactly the same degree of resonance would occur in each, especially in view of the formal positive charge on nitrogen when structures like I. and II. above are formulated for the nitroso group. It has been observed in nitrogen compounds¹⁰



that structures having adjacent like charges usually make much smaller contributions to the normal state than those having a different distribution of charges. That structure III. does make an appreciable contribution is demonstrated by the observed shortening of the N—O distance below the double bond value; but since the degree of shortening appears to be less than in the C—O bond there is some probability that in the M—N—O group the relative contributions of the two structures is displaced in the direction required by the adjacent charge rule.

The objection might be raised that, since a shortening of interatomic distances is found also in the non-metallic halides,¹¹ an explanation might be found in that the values adopted for the radii of the central atoms are in all cases in error, as an alternative to the resonance shortening postulated to explain the effect. It is the view of the authors that such an alternative explanation is not applicable: in the case of the non-metallic halides it was shown that no consistent values can be found for the atomic radii which do away with the shortening. The values adopted here for the radii of Fe, Co and Ni are unlikely to be in error by an amount sufficient to invalidate our conclusions, since in tetrahedral compounds where only *s* and *p* orbitals are involved, the radii will be expected to be, if anything, larger than in the sulphide structures on which the quoted values are based, which involve *d*, *s* and *p* orbitals. It may be noted that a pronounced and exactly parallel shortening has been observed by Rüdalt and Hofmann¹² in the C—O distance of chromium hexacarbonyl (calc. 2.02 Å, found 1.80 Å). Since the bond forming orbitals

¹⁰ L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, 1937, 59, 13.

¹¹ L. O. Brockway and Wall, *ibid.*, 1934, 56, 2373.

¹² Rüdalt and Hofmann, *Z. physik. Chem.*, B, 1935, 28, 351.

of this octohedral compound are of the same type as in the compounds forming the basis of the standard single-bond covalent radius, the uncertainty is here reduced to a minimum. The shortening observed thus lends additional confirmation to the views we have developed in this paper.

In this connection it is interesting to note the statement of Sidgwick and Bailey³ that "the suggestion that the NO is doubly linked to the metal cannot be entertained." The large difference between the observed distances and the sums of the single bond radii, however, now make it evident that structures of both kinds (*i.e.*, having both single and double bonds, respectively, on the central atom) are important in the metal carbonyls.

Summary.

The molecular structures of $\text{Fe}(\text{NO})_2(\text{CO})_2$ and $\text{Co}(\text{NO})(\text{CO})_3$ have been investigated by the electron diffraction of the vapours with the results shown in Table III. The bonds from metal to carbon and nitrogen, respectively, are observed to be about 0.16 Å. less than the sum of the single bond covalent radii while the bond lengths in the carbonyl and nitroso groups are intermediate between double and triple bonds. These observations are compared with earlier ones for $\text{Ni}(\text{CO})_4$, and the resonating electronic structure proposed for the nickel compound is considered to be valid for the iron and cobalt compounds, also.

Contribution No. 598.

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A PHOTOELECTRIC METHOD OF MEASURING p_{H} VALUES WITH INDICATOR SOLUTIONS.

By G. F. LOTHIAN.

Received 17th June, 1937.

Indicators change their colour with change of p_{H} value by reason of a change in a definite absorption band in the visible spectrum. Brode¹ has shown that for the common indicators as the p_{H} value changes, the absorption band changes in density without change of its wavelength, and has shown how p_{H} values may be determined by measuring the density of absorption at the peak of the band, using a visual spectrophotometer.

The method here to be described is a development of this, being based on the measurement of the absorption of an indicator solution over a finite band of wavelengths transmitted by a filter. In this way it is possible to use a simpler measuring instrument than the spectrophoto-

¹ Brode, *J. Amer. Chem. Soc.*, 1924, 46, 581.

meter used by Brode. The filter for use with a given indicator should be chosen so that it transmits light at the wavelengths covered by the absorption band of the indicator.

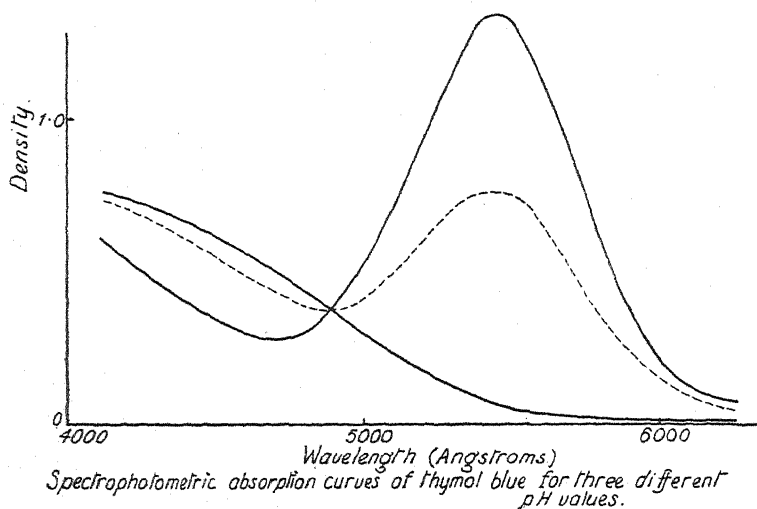


FIG. 1.

The method of choosing the best filter for use with an indicator may be described with reference to thymol blue. When the p_H varies from 2.3 to

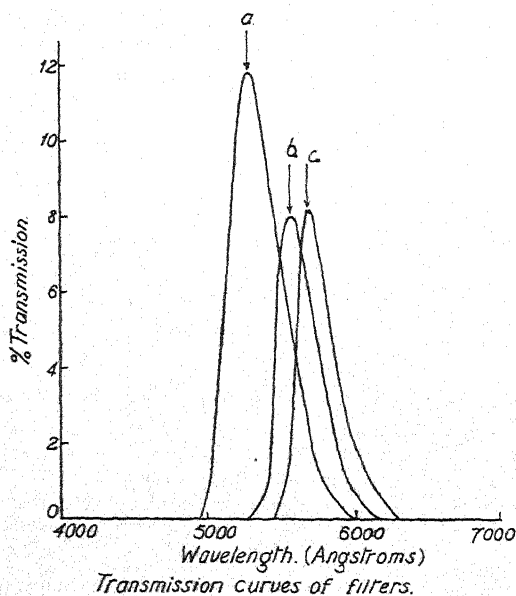


FIG. 2.

1.2 the colour of this indicator changes from yellow to purple, due to the development of an absorption band with a peak at a wavelength of about 5450 Å.

Fig. 1 shows the absorption of this indicator for p_H values corresponding to the extremes of the range and an intermediate p_H value. It is obvious from the figure that it is possible to determine a p_H value with this indicator by measuring the absorption of a given concentration of indicator at a wavelength band near the peak.

The curves of Fig. 1 show that the variation of absorption with p_H value is greatest at the peak of the band. A

filter transmitting a narrow range of wavelengths near the peak of the absorption band would therefore give the greatest density variation. In practice such a filter transmits so small an amount of light, however, that

it is not possible to measure the densities accurately. It has therefore been found more accurate to use a filter transmitting a wider range of wavelengths. A filter of this type transmits light at the sides of the absorption band of the indicator where the density variation is smaller than at the peak; the smaller density variation to be determined can, however, be measured more accurately, and it is found that with the instrument used for the measurements given below there is an overall gain in sensitivity by using a filter of reasonably wide transmission band. On the other hand, if the transmission band of the filter extends beyond the region of the absorption band—in the case of the indicator of Fig. 1—to wavelengths shorter than 4900 or longer than about 6000 Å, there will be a loss of sensitivity.

Working on these lines, three filters transmitting spectral ranges suitable for use with a number of indicators have been made from commercial glass and gelatine filters. The transmissions of these filters are shown in Fig. 2. They are made up of the following components:—

- a. Wratten² filters 12 and 58A and Chance³ Blue Green Glass No. 6.
- b. Wratten² filters 21 and 58 and Chance³ Blue Green Glass No. 6.
- c. Wratten² filters 22 and 59 and Chance³ Blue Green Glass No. 6.

The function of the Chance glass is to absorb light at the far red end of the spectrum which is transmitted by gelatine filters and which might cause large errors in photo-electric measurements.

Measurements were made on a number of indicator solutions using one or the other of these filters in conjunction with the Hilger Spekker Photoelectric Absorptiometer.⁴ This instrument consists of a light source, colour filter, test solution, photoelectric cell (of the rectifier type) and galvanometer. The absorption of the test solution is matched against an adjustable aperture which is calibrated directly in densities. A second photo-electric cell connected differentially with the first makes a null point circuit with its attendant advantages.

As an example of the use of the method, a set of measurements was made with methyl red in a number of buffer solutions of known p_H value, using the filter (a) above. The technique used was to mix $\frac{1}{2}$ c.c. of indicator with $9\frac{1}{2}$ c.c. of buffer solution, each measured accurately from a graduated pipette, and to measure the absorption on the Spekker Absorptiometer. The results obtained are shown in the curve of Fig. 3.

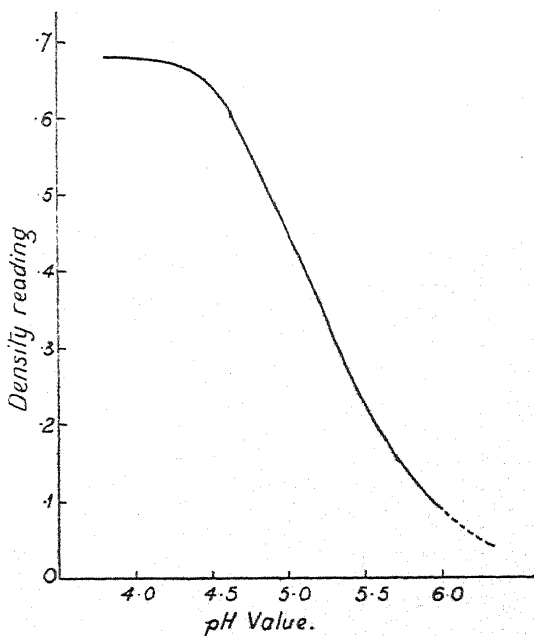


FIG. 3.—Curve showing variation of absorption of methyl red indicator with p_H value, as measured by the Spekker Absorptiometer.

² Wratten Light Filters, published by Kodak, Ltd.

³ Chance Parsons Colour Filters, published by Chance Bros. & Co. Ltd.

⁴ J. Sci. Inst., 1936, 13, 268.

The error of measurement of absorption on the instrument is in this case rather less than 0.01 units of density, corresponding to an error of p_H determination of less than 0.025 at the centre of the range of the indicator. Such a curve forms a calibration for use in the determination of p_H values of unknown solutions.

A number of other indicators were measured on the absorptiometer with suitable filters, only the two extreme colours corresponding to the limiting p_H values being measured. In each case, the indicator was used in a concentration of $\frac{1}{2}$ c.c. of the standard commercial indicator solution in 10 c.c. From the sensitivity of the measurements, determined for each indicator, the mean precision with which a p_H value can be measured was found. At the centre of the range of the indicator (corresponding to the steepest part of the curve as shown for methyl red in Fig. 3), the sensitivity will be greater than this mean value.

The results of these measurements are set out in the table. The last column shows the mean precision obtainable—varying from 0.02 to 0.04 for different indicators.

Indicator.	Filter.	Nominal p_H Range.	Corresponding Range of Density Readings.	Mean Precision of p_H Determination.
Thymol Blue . . .	<i>a</i>	1.2-2.3	0.90-0.07	0.02
Bromophenol blue . . .	<i>c</i>	2.8-4.4	0.02-1.28	0.04
Methyl red . . .	<i>a</i>	4.0-6.4	0.68-0.04	0.04
Bromo cresol purple . . .	<i>c</i>	5.2-6.8	0.01-1.26	0.02
Bromo thymol blue . . .	<i>c</i>	6.0-7.6	0.0-0.94	0.02
Phenol red . . .	<i>b</i>	6.8-8.4	0.0-0.74	0.02
Cresol red . . .	<i>c</i>	7.2-8.8	0.015-0.90	0.02
Thymol blue . . .	<i>c</i>	8.0-9.6	0.02-1.13	0.03

The concentrations of indicator used are such that the absorptiometer readings obtained in the middle of the p_H range correspond to the values which can be measured most accurately on a photoelectric instrument (*viz.* a density reading⁵ of about 0.3-0.6). Where it is required to measure to the greatest accuracy a p_H value not in the middle of the range, a concentration of indicator should be used to give, for the p_H value being determined, an absorption reading in the range 0.3-0.6.

The method can be extended to determine the p_H values of coloured solutions by measuring the absorption of solution plus indicator compared with solution alone. The calibration curve showing p_H value against density reading will be modified by the presence of the coloured solution, and it would be necessary to determine the calibration curve for the indicator with a second cell of the coloured solution in the light beam of the measuring instrument.

The method of p_H determination here described has the following advantages:—

- (1) It is not necessary to maintain standard solutions against which to match the test solutions as is the case with the Duboscq colorimeter for example. The calibration with standard solution needs only to be made once.
- (2) The method is independent of the visual judgment of colour match, and it gives a good precision of measurement.
- (3) A photoelectric instrument gives most accurate measurement for a small absorption (see above) so that a small quantity of indicator is

⁵ Twyman and Lothian, *Proc. Physic. Soc.*, 1933, 45, 643.

sufficient to give accurate measurement. This is an advantage in the measurement of weakly buffered solutions, where the addition of indicator may change the p_H value being measured.

Acknowledgment is due to Dr. H. Moore for the use of the laboratory of the British Scientific Instrument Research Association for making some of these measurements, and to Messrs. Adam Hilger Ltd. for permission to publish these results.

Summary.

A method is described for the precise determination of p_H values with indicators, by means of photoelectric measurement of light absorption. The conditions for obtaining the greatest precision are elaborated, and results are given for methyl red.

*Adam Hilger Ltd.,
London.*

THE PROPERTIES OF DETERGENT SOLUTIONS.

By J. POWNEY AND C. C. ADDISON.

Received 9th June, 1937.

PART II. THE SURFACE AND INTERFACIAL TENSIONS OF AQUEOUS SOLUTIONS OF ALKYL SODIUM SULPHATES.

The present investigation is concerned with the measurement of surface and interfacial tensions of aqueous solutions of pure sodium alkyl sulphates having chain lengths of from twelve to eighteen carbon atoms. These compounds show less tendency to hydrolyse than do the normal carboxylic soaps, and they are therefore more suitable as media for the study of the surface and general properties of colloidal electrolyte solutions. Furthermore, compounds of this type have recently become of importance as detergents and wetting agents. The data recorded here have been obtained under conditions of temperature and concentration normally met with in detergent processes.

Lottermoser and Stoll¹ have previously shown that solutions of certain of these alkyl sulphates exhibit sharp changes in surface tension over narrow concentration ranges which are dependent upon chain length and temperature. No well-defined breaks in interfacial tension curves have until now been observed. In the present work a close agreement between surface and interfacial tension data for these paraffin-chain salts has been found. Both sets of curves show abrupt changes at critical concentrations which correspond to breaks in the electrical conductivity curves obtained for the same substances by Lottermoser and Puschel² and by Howell and Robinson.³

The results are discussed in the light of Murray's theory⁴ that the single long-chain ions are mainly responsible for the surface activity.

¹ Lottermoser and Stoll, *Koll. Z.*, 1933, 63, 49.

² Lottermoser and Puschel, *ibid.*, 1933, 63, 175.

³ Howell and Robinson, *Proc. Roy. Soc. A*, 1936, 155, 386.

⁴ Murray, *Trans. Faraday Soc.*, 1935, 31, 206.

Experimental.

Materials.—Sodium dodecyl, tetradecyl, hexadecyl and octadecyl sulphates were prepared from the corresponding pure alcohols by a modification of the method described by Lottermoser and Stoll.¹ The alcohols used had correct melting points, and distillation at low pressure produced no change in melting point. The alkyl sulphates so obtained contained small amounts of sodium sulphate and free long-chain alcohols. They were purified by repeated crystallisation from ethyl alcohol and from water. The resulting products were treated for at least eight hours in a Bolton and Revis Extractor, with petroleum ether (boiling point, 40°-60° C.). This procedure was found to be very effective for removing the last traces of unesterified long-chain alcohols. The esters finally obtained were pure white, and gave clear solutions in water. As the chain length increased a marked falling off in crystalline form and solubility was apparent. Measurements of p_H , made with a glass electrode system, showed that the products gave neutral solutions in water.

The solutions used for any individual series of readings were obtained by dilution of a single stock solution. The distilled water used throughout the work was free from carbon dioxide, and was prepared in a Hartley Still* and collected in Pyrex vessels. Its specific conductivity was $K_{18} = 1.15 \times 10^{-6}$ ohms⁻¹ cm.⁻¹, and a daily check was kept on this value.

Surface Tension Measurements.—Surface tension measurements were made by means of a Du Noüy tensiometer. The original platinum ring was replaced by one made from a platinum-iridium alloy, as this was found to be less subject to deformation. A specially designed air thermostat provided with means of controlling the humidity at any desired value was used. When working at high temperatures it is essential that the rate of evaporation should be kept low, and preferably constant, if reproducible values of surface tension are to be obtained. If evaporation is considerable, then the true surface temperature of the solution may differ considerably from the measured bulk temperature, and fluctuations in the rate of evaporation may cause corresponding changes in the surface tension values. The solution being investigated was enclosed in a second chamber within the thermostat, and any leakage of air into this chamber was at a controlled and high relative humidity. The torsion balance was mounted on the outside of the thermostat, the suspension carrying the ring being passed through a small aperture in the top. This necessitated the use of an electrical heater round the suspension at the point where it emerged from the thermostat, in order to prevent local condensation of moisture. The temperature and relative humidity could be controlled to $\pm 0.2^\circ$ C. and ± 2 per cent. R.H. respectively, over the range 30°-85° C. Vibration was reduced to a minimum by mounting the thermostat (approx. 250 lbs.) on concrete pillars with suitable rubber insulation. The recorded temperatures refer to those measured in the solution under examination. The following procedure was adopted throughout this work. All solutions were preheated to 85° C. in Pyrex vessels and placed in the thermostat, also maintained at this temperature. The thermostat temperature was then slowly decreased in stages of approximately 5° C., the rate of cooling being 10° C. per hour, and five surface tension determinations made at each temperature level. The variations in the readings were not greater than ± 0.2 dyne/cm., except in certain very dilute solutions where variations up to ± 0.5 dyne/cm. were sometimes recorded. Each set of readings for any particular concentration required about five hours to complete, but changes in concentration due to evaporation were negligible over this period.

Interfacial Tension Measurements.—Interfacial tensions against xylene were measured by the drop weight method. Drops of xylene were allowed to flow from the pipette into a large volume (200 c.c.) of the alkyl

* H. Hartley, *J.C.S.*, 1908, 428T.

sulphate solution. The same stock of xylene (B.Pt. = 139° C., Messrs. Griffin & Tatlock's "Pure") was used throughout this work. Its density was measured over the temperature range 20° – 80° C. and varied from 0.8524 at 20° C. to 0.8011 at 80° C.

Criticism has frequently been directed against the drop weight method of determining the interfacial tensions of solutions of normal soaps, owing to the appreciable migration across the interface of the fatty acid produced by hydrolysis. No such difficulties were encountered in working with the alkyl sulphates, which do not hydrolyse under the experimental conditions employed, and whose solubility in xylene, even at the higher temperatures, is negligible.

In view of the large range of interfacial tensions investigated, and consequently the wide variation in the number of drops of xylene which would be obtained from a fixed volume, a special drop pipette was designed having a series of three calibrated bulbs A, B and C (Fig. 1) of volume 0.21 c.c., 1.00 c.c. and 5.27 c.c. respectively. The jet had an internal diameter of 0.059 cm., and was prepared in the manner recommended by Harkins and Brown.⁵ The use of the appropriate bulb rendered it unnecessary to count more than about 100 drops for any one determination. The use of the smallest bulb with the jet described above enabled tensions of the order of 1 dyne to be measured in a relatively short time, and with a high accuracy. Results could be reproduced to one drop, giving, over the whole range of tension, an experimental error of less than ± 1 per cent.

The method of controlling the rate of drop formation was that used in a previous investigation,⁶ and consisted of a calibrated series of fine air leaks drawn from glass capillary and attached directly to the top of the pipette. Since the measurements permitted the use of very small shallow bulbs, the change in head of pressure, and consequently the change in time of formation of a drop was negligible throughout any experiment. It was therefore possible to deduce the drop number directly from the drop rate, and the total time taken to empty the bulb. The bulbs were enclosed in a jacket D, through which water at a constant temperature of 20° C. $\pm 0.5^{\circ}$ C. was circulated. The bulbs were thus maintained at a constant volume irrespective of the temperature at the jet. The lower end of the pipette was made of fine capillary tubing, which was connected, under the level of the solution in flask E, to a short length of wider tubing which terminated in the jet. Under these conditions no expansion of the xylene took place until it was under the surface of the aqueous solution. The flask E containing the solution under test was surrounded by an electrically heated water bath, maintained at the required temperature. The temperature control of the test solution at the higher temperatures was accurate within $\pm 1^{\circ}$ C., and the rate of flow was so slow that the xylene emerging from the jet was already preheated to the temperature of the solution. An air vent F passing through the cold water jacket D also served to condense any xylene evaporating from the surface at the higher temperatures.

It was necessary to apply two correction factors for changes in density with temperature, namely, an allowance for the expansion of the xylene

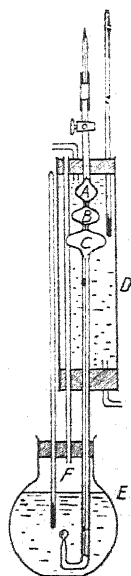


FIG. 1.—Modified drop pipette for measuring interfacial tensions at various temperatures.

⁵ Harkins and Brown, *J.A.C.S.*, 1919, **41**, 499.

⁶ Gibby and Addison, *J.C.S.*, 1936, **119**, 1306.

between bulb and jet, since all drop numbers originally referred to a fixed volume of liquid at 20° C., and for the change in the density difference between solution and xylene with temperature.

Interfacial tensions were calculated from the drop weight by the use of the correction factors derived by Harkins and Brown.⁵

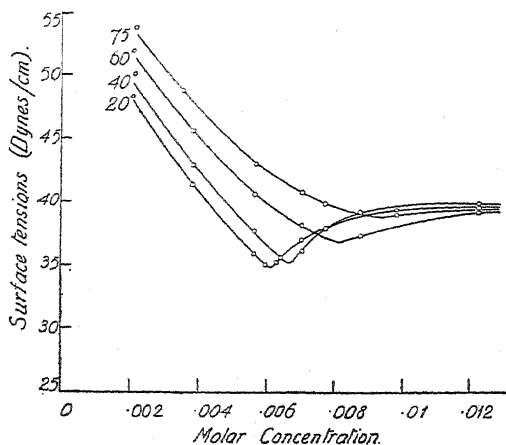


FIG. 2.—Surface tension-concentration curves for sodium dodecyl sulphate.

Results and Discussion.

The surface tension data for dilute solutions of sodium dodecyl, tetradecyl, hexadecyl and octadecyl sulphates have been determined over the temperature range 30°-80° C. and are given in Figs. 2 to 5 respectively. The interfacial tensions over the same range of chain length have been determined at

60° C. (Fig. 6). In the case of sodium dodecyl sulphate, interfacial tension data have also been obtained for the temperature range 20°-75° C. (Fig. 7).

Time Factor.

In view of the recent observations of Adam and Shute,⁷ Reed and Tartar,⁸ and Lottermoser and Giese⁹ that the surface and interfacial tensions of solutions of certain long-chain colloidal electrolytes slowly change with time, it is necessary to emphasise that the data recorded in the present paper refer to fairly fresh surfaces. Normally, surface tension measurements were made within a few minutes of forming the surface, but it

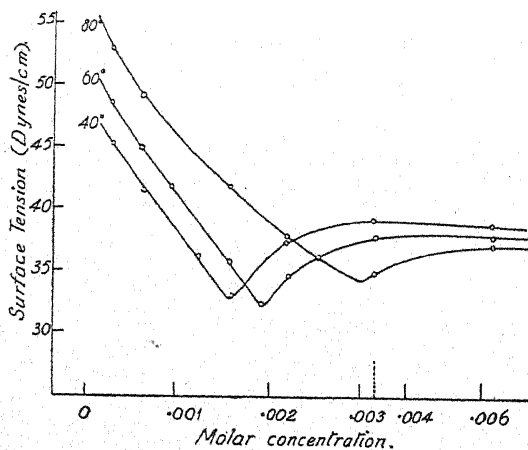


FIG. 3.—Surface tension-concentration curves for sodium tetradecyl sulphate.

⁷ Adam and Shute, *Trans. Faraday Soc.*, 1935, 31, 204.

⁸ Reed and Tartar, *J.A.C.S.*, 1936, 58, 322.

⁹ Lottermoser and Giese, *Koll. Z.*, 1935, 73, 155, 276.

was found in preliminary experiments on a number of different alkyl sulphate solutions, that if the ring was placed in the surface and allowed to remain for periods of from one to fifteen hours, and then slowly withdrawn, the surface tension values so obtained did not differ by more than the experimental error from those obtained with surfaces a few minutes old. The only comparable data is that of Lottermoser and Giese,⁹ who found changes of surface tension with time for a few concentrations of sodium dodecyl sulphate at room temperature. It is probable that the abnormal concentration or even crystallisation of surface active material on the platinum ring and exposed glass surface, suggested by Lottermoser and Giese as a possible explanation, does not occur when precautions are taken to reduce evaporation to a minimum by working at high humidities.

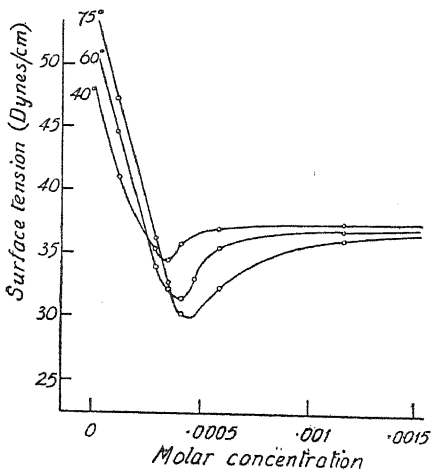


FIG. 4.—Surface tension-concentration curves for sodium hexadecyl sulphate.

From general considerations of the forces producing dipole orientation at an interface, it might be expected that the substitution of an organophilic liquid for air at the phase boundary would result in a more rapid establishment of orientation

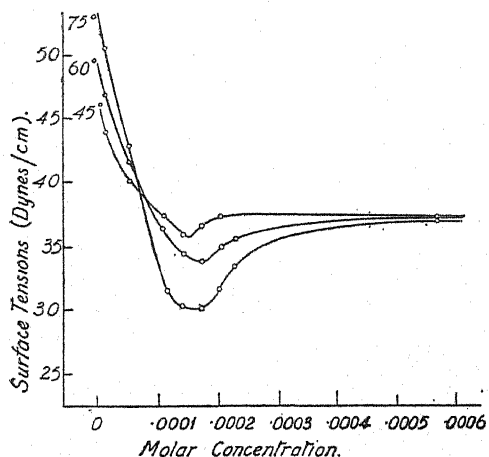


FIG. 5.—Surface tension-concentration curves for sodium octadecyl sulphate.

equilibrium. In the case of interfacial tensions, therefore, preliminary experiments were carried out to determine the minimum time required for the formation of a drop to ensure that equilibrium conditions were obtained. In his original experiments Tate¹⁰ quoted 40 seconds for each drop release as the minimum time necessary for equilibrium. It is interesting to note, however, that other investigators, e.g. Lewis¹¹ and Lord Rayleigh¹² have found this time unnecessary, and Lewis suggests 12 to 15 seconds per drop

as a necessary minimum time. Although for certain sulphonate solutions

¹⁰ Tate, *Phil. Mag.*, 1864, **27**, 176.

¹¹ Lewis, *ibid.*, 1908, **15**, 499; 1909, **17**, 466.

¹² Lord Rayleigh, *ibid.*, 1899, **48**, 321.

Reed and Tartar⁸ observed a slow drift in interfacial tension with time, their results show that in the majority of cases no appreciable change took place over a considerable period. In the present investigation reproducible readings were obtained if the drops were given at least 12 to 15 seconds to form, this minimum time varying slightly with the size of the drop formed. No alteration in interfacial tension was observed

if longer periods were allowed. Furthermore, it was found that no change in the nature of the bulk solution of these paraffin-chain salts took place with time. Drop numbers taken through solutions only a few minutes old were still reproducible after the solutions had been left to stand for several weeks.

Whilst the slow drifts of surface tension over periods up to several weeks recorded by Reed and Tartar, and Adam and Shute, are of great interest, it would seem that until an explanation of this phenomenon is established, it is not unreasonable to assume that the reproducible surface tension data for alkyl sulphate solutions recorded here for fairly fresh surfaces are representative of a true surface adsorption equilibrium. In view of the recently observed sensitivity of surface phenomena to traces of foreign electrolytes,^{13, 14, 15} it is possible that over these abnormal periods of time, contamination of the solutions under examination by electrolytes from the containing vessel may be sufficient to account for such changes.

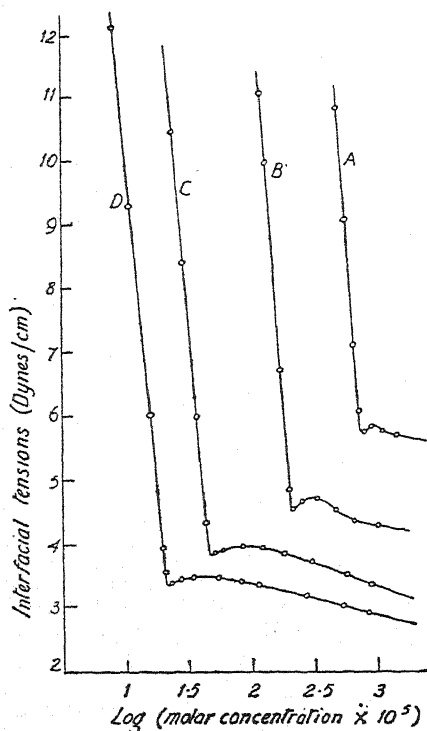


FIG. 6.—Interfacial tensions at 60° C.

- A Sodium dodecyl sulphate.
 B „ tetradecyl „
 C „ hexadecyl „
 D „ octadecyl „

Critical Concentrations for Micelles.

The curves exhibit well-defined breaks at certain critical concentrations, which are dependent upon temperature and chain length. Other physical properties of colloidal electrolyte solutions (*e.g.* densities¹⁶ and electrical conductivities^{2, 3}) are known to exhibit similar abrupt changes. According to Bury¹⁶ and collaborators, such breaks probably correspond to a sharp transition in bulk solution from single ions to

¹³ Harkins and Myers, *Nature*, 1937, 139, 367.

¹⁴ Rideal, Mitchell and Schulmann, *ibid.*, 1937, 139, 625.

¹⁵ C. Robinson, *ibid.*, 1937, 139, 626.

¹⁶ Bury and collaborators, *Phil. Mag.*, 1927, 4, 841; *J. Chem. Soc.*, 1929, 679; 1930, 2263.

micelles, and the concentrations at which the breaks occur have conveniently been termed "Critical Concentrations for Micelles." Whilst Lottermoser and Stoll¹ have previously found abrupt changes in surface tension curves for sodium dodecyl and tetradecyl sulphates, their curves for the hexadecyl, and particularly the octadecyl salt, bear little resemblance to those for the two lower members, and exhibit no well-defined breaks. The present investigation of the hexadecyl and octadecyl salts, however, at concentrations lower than those investigated by Lottermoser and Stoll, reveals abrupt changes of the same type as those found for the dodecyl and tetradecyl sulphates.

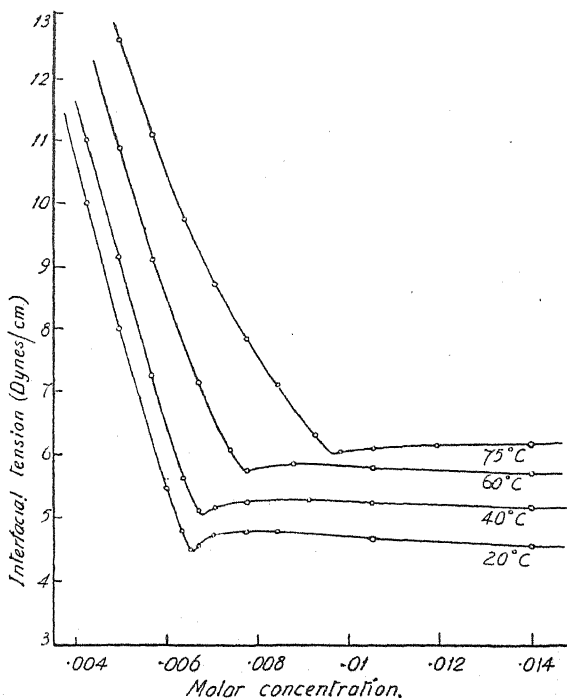


Fig. 7.—Interfacial tension-concentration curves for sodium dodecyl sulphate.

Values of critical concentrations now obtained by both surface tension

TABLE I.—VARIATION IN CRITICAL CONCENTRATIONS OF ALKYL SULPHATE SOLUTIONS WITH CHAIN LENGTH.

Paraffin-Chain Salt.	Critical Concentrations (Molar) at 60° C.		
	From Surface Tensions.	From Interfacial Tensions.	From Conductivity Data.
$C_{12}H_{25}SO_4Na$	0.008 0.007 *	0.0077	0.009 † 0.0076 ‡
$C_{14}H_{29}SO_4Na$	0.002 0.0022 *	0.0021	0.0026 ‡
$C_{16}H_{33}SO_4Na$	0.00043	0.00047	0.001 † 0.00076 †
$C_{18}H_{37}SO_4Na$	0.00017	0.00022	0.00039 ‡

* Derived from Lottermoser and Stoll's data.¹

† Howell and Robinson.³

‡ Lottermoser and Puschel.²

conductivity $K_{18} = 1.15 \times 10^{-6}$ ohms⁻¹ cm.⁻¹. It is possible that by

and interfacial tension measurements are in close agreement one with another, and agree reasonably well with those indicated by electrical conductivity measurements (Table I.).

In a forthcoming contribution it is hoped to discuss in detail the considerable lowering of critical concentration brought about by foreign electrolytes. The values given in Table I. refer to data obtained in water having a specific

using even better water the critical concentrations may be very slightly increased.

Nature of Surface Active Species.

Although considerable advances have been made in recent years concerning the constitution of aqueous solutions of paraffin-chain salts, there is at present no complete agreement as to the nature of the species responsible for their surface activity. Lottermoser and Stoll¹ have assumed in the interpretation of their surface tension data for alkyl sulphates, that medium sized aggregates of undissociated salt have the greatest surface activity. This view is also shared by Reed and Tartar⁸ from considerations of surface tension data for paraffin-chain sulphonates. On the contrary, Murray⁴ has suggested that single long-chain ions are mainly responsible for the surface activity of colloidal electrolyte solutions, and that the surface activity of the ionic micelles is negligible. A concise study of the equilibrium existing between single long-chain ions and micelles in aqueous solutions of paraffin-chain salts has recently been presented by Hartley.¹⁷ Traube¹⁸ has also expressed the view that surface activity is influenced almost exclusively by non-colloidal particles.

By applying the Mass Action equation to the case of an electrolyte aggregating to form micelles, Murray⁴ has shown that with increasing solute concentration, the absolute concentration of single long-chain ions shows an initial rapid increase. At higher concentrations this is followed by a decrease due to the sudden aggregation to form micelles, and finally by a slight tendency to increase again. If the surface activity is determined by the single long-chain ions, it might be expected that this behaviour would be reflected in surface and interfacial tension data. The close resemblance which is actually found between the form of the surface and interfacial tension curves, and that of the theoretical curve connecting concentration of long-chain ions and total solute concentration, may be regarded as evidence in support of this view. Further evidence is provided by the observation of Howell and Robinson³ that up to the critical concentration the alkyl sulphates are completely dissociated in solution. Since over this same concentration range the lowerings of surface and interfacial tensions attain almost their maximum values, considerable surface activity must be attributed to the single long-chain ions. The slight variations in tension at concentrations above the critical can be regarded as due to micelles only in so far as they affect the concentration of single ions present.

Effect of Temperature and Chain Length on Surface Activity.

Sufficient data have been obtained to enable a fairly accurate estimate to be made of the magnitude of the change in critical concentration with temperature for the alkyl sulphates (Table II.).

It will be seen from Table II. that over the range of chain length from 12 to 18 carbon atoms the temperature coefficient is below 2.5 per cent. per degree. The coefficient rises to a maximum for a C₁₄ chain, and thereafter falls off rapidly with increasing chain-length. The temperature coefficients obtained for the dodecyl salt from both

¹⁷ Hartley, *Aqueous Solutions of Paraffin-Chain Salts*, Hermann et Cie, Paris, 1936.

¹⁸ Traube, *Trans. Faraday Soc.*, 1935, **31**, 1730.

TABLE II.—TEMPERATURE COEFFICIENT OF CRITICAL CONCENTRATION.

Paraffin-Chain Salt.	Temperature Range °C.	Limits of Critical Concentration (Molar).	Temperature Coefficient Per Cent. per Degree.
$C_{12}H_{25}SO_4Na$	40-75	0.0066-0.0096 *	1.3
	40-75	0.0066-0.0094	1.2
$C_{14}H_{29}SO_4Na$	40-80	0.0015-0.0028	2.2
$C_{16}H_{33}SO_4Na$	40-75	0.00033-0.00047	1.0
$C_{18}H_{37}SO_4Na$	45-75	0.000156-0.000172	0.35

* From interfacial tension data.

surface and interfacial tensions agree well with one another, and with the value (about 1 per cent. per degree) calculated from Howell and Robinson's conductivity data,³ while the value for the tetradecyl sulphate approximates to the 2 per cent. per degree found by Hartley for cetane sulphonic acid.¹⁹ The rapid falling off in the case of the higher alkyl sulphates is in accord with similar figures calculated from the conductivity data of Lottermoser and Puschel.²

From Table I. it is apparent that Traube's rule will hold if applied to the change with chain length of a bulk property such as critical concentration, although the change in surface activity with chain length, as determined by the lowering of surface tension or of interfacial tension, will not necessarily follow this rule. In the case of interfacial tension it is clear that there is an additional force operating in the orientation of the amphipathic molecules in the surface layer, namely the attraction of the organic phase for the hydrocarbon chain.⁶ Thus, whilst the interfacial activity shows a steady increase with chain length, the surface activity passes through a maximum, and the chain length at which this maximum occurs depends on the temperature.

The change in surface and interfacial activity with temperature can be attributed to at least two opposing factors. Thus, whilst an increase in temperature will bring about a decrease in the adsorption of the long-chain ions, any dissociation of micelles at higher temperatures will lead to an increase in the bulk concentration of surface active species. The influence of this latter effect must be the same on surface and interfacial tension, since it is essentially a bulk phenomenon, although it is highly probable that considerable differences exist between the heats of adsorption of surface active material at an air-solution and at an oil-solution interface. In dilute solutions of tetradecyl sulphate, for example, the effect of increasing temperature is to increase the surface tension. At high concentrations, however, the micellar dissociation effect becomes predominant, and results in a lowering of tension with increasing temperature. Evidence has been obtained that the same effect occurs in interfacial tensions. In addition the experimental curves indicate that a gradual adjustment in the balance between these two effects takes place with varying chain length. In the case of the C_{18} salt, for example, the concentration (with respect to the critical) at which the two effects balance is considerably less than the corresponding value for the C_{16} salt. It would seem from these considerations

¹⁹ Hartley, *J.A.C.S.*, 1936, 58, 2437.

that the temperature coefficient of adsorption increases with decreasing chain length. Thus the interfacial activity of the C_{12} salt is almost completely determined by this factor, although the thermal dissociation of the micelles results in a much smaller tension difference between the extreme temperature curves in micellar solutions than occurs below the critical concentration.

The Applicability of the Gibbs Theorem.

Numerous difficulties are involved in the direct application of the Gibbs Theorem to surface and interfacial tension data for colloidal electrolyte solutions.^{20, 11, 6} The anomalous conclusions often arrived at are to be attributed to the operation of various disturbing factors expressly excluded in the derivation of the Gibbs Equation. It is generally agreed that the presence of a potential difference at any interface must invalidate the applicability of the Gibbs Theorem. Although Lewis¹¹ has suggested a modified form of the equation which includes a term depending on the potential difference across the interface, no satisfactory mechanism has so far been suggested to explain precisely what influence this potential difference has on the adsorbed molecules. McBain and Wilson²¹ have recently pointed out that a paradox arises when the Gibbs Theorem is applied to surface tension data for soap solutions, since over certain regions the surface tension increases with increasing total concentration of soap, which apparently indicates that the surface adsorption is negative while the surface activity is almost at its maximum. McBain²² has suggested that the rise in tension with increasing concentration might be explained by the decreasing electrical repulsions in the adsorbed layer resulting from the aggregation to form micelles. Although this effect must be partly responsible, the assumption that single ions constitute the surface active species, also affords a tenable explanation of this rise. It is probable that decrease in surface activity with increasing total concentration of solute is due to the decrease in bulk concentration of surface active species due to their rapid aggregation to form micelles, rather than to negative adsorption. In fact, as Nickerson²³ has suggested, negative values of adsorption would probably not arise if the concentration function were differentiated, and each species considered as a separate solute. Owing to the lack of further information concerning these very significant disturbing factors, it was considered that any attempt to deduce adsorption data for these systems by applying Gibbs' equation would serve no useful purpose.

Summary.

Surface tension data for dilute solutions of paraffin-chain sulphates have been determined by the ring method, and are recorded over a wide range of temperature. Interfacial tensions against xylene have been measured by the drop weight method, and are recorded for the same salts at 60° C. Interfacial tensions for sodium dodecyl sulphate solutions are given over the temperature range 20°-75° C.

Both surface and interfacial tension curves show well defined breaks at certain critical concentrations. The nature of the surface active species,

²⁰ McBain and Davies, *J.A.C.S.*, 1927, 49, 2230.

²¹ McBain and Wilson, *ibid.*, 1936, 58, 379.

²² McBain, Ford and Wilson, *Koll. Z.*, 1937, 78, 1.

²³ Nickerson, *J. Physic. Chem.*, 1936, 40, 277.

and the equilibrium between simple long-chain ions and micelles, are discussed with particular reference to the work of Murray and Hartley.

The influence of chain length on the temperature coefficients of both surface and interfacial tensions and critical concentrations are discussed, and the various disturbing factors which render inadvisable the application of Gibbs' equation to data for these solutions are given.

PART III. THE INFLUENCE OF ADDED ELECTROLYTES ON THE SURFACE ACTIVITY OF THE HIGHER ALKYL SODIUM SULPHATES.

During the course of the investigation reported in Part II. it was observed that traces of certain inorganic impurities could considerably modify the interfacial tension values obtained. It was subsequently found that the effect was common to the air-solution interface also. A detailed study of the influence of various added salts on both surface and interfacial tension has therefore been undertaken.

The extreme sensitivity of surface phenomena to traces of metallic contamination has recently been emphasised by Harkins and Myers,¹³ Mitchell, Rideal and Schulmann,²⁴ and Robinson.¹⁵ The last author has shown that the interfacial tensions of "Igepon T" and of sodium cetyl sulphate against oil are influenced by salt addition, there being a marked valency effect. Hartley¹⁷ has shown in connection with indicator displacement phenomena, that the effect of the addition of ordinary electrolytes to solutions of colloidal electrolytes such as cetyl pyridinium chloride, is to depress the critical concentration.

The results now obtained for alkyl sodium sulphate solutions containing known concentrations of added electrolytes, show that sodium salts, and particularly calcium salts, bring about a considerable lowering of critical concentration and of surface and interfacial tension values.

Results and Discussion.

The apparatus used in the present investigation was identical with that previously described,²⁵ except that a suitable source of illumination was provided in order to detect turbidity.

Influence of Added Sodium Salts.

The interfacial tensions, against xylene, of sodium dodecyl sulphate solutions containing various concentrations of added NaCl, have been measured at 20° C. (Fig. 8). The curves show clearly that

(a) a progressive and very considerable lowering of critical concentration occurs with increasing addition of NaCl. Thus, in the presence of 1 per cent. NaCl (1 per cent. = 0.171 Molar NaCl), the critical concentration is reduced from 0.00645 to 0.00105 M. Higher concentrations of NaCl could not be used, as salting-out occurred.

(b) On the addition of up to 1 per cent. NaCl, a progressive decrease from 4.5 dynes/cm. to 1.7 dynes/cm. occurs in the minimum interfacial tension values obtained.

(c) The sensitivity of interfacial tensions to added NaCl is much greater in dilute solutions below the critical concentration than in the micellar region.

²⁴ Mitchell, Rideal and Schulmann, *Nature*, 1937, **139**, 625.

²⁵ This vol., p. 1243.

(d) Interfacial tension minima, which occur at the critical concentrations become increasingly accentuated as the concentration of NaCl increases.

Robinson⁴ has shown that the influence of added salts on the interfacial tension of solutions of substances having a surface active anion is solely due to the added cation. The present results support this view. In preliminary experiments, values almost identical with those given for NaCl were obtained by the addition of equivalent concentrations of other sodium salts, and were quite independent of the nature of the associated

anion. Sodium dihydrogen phosphate, sodium borate, sodium sesquicarbonate and trisodium phosphate were used, and although the p_H varied from 4.5 to 12, the effect of this variation on the tension values was negligible.

In order to determine whether these effects were independent of chain length, a similar series of experiments was carried out with sodium octadecyl sulphate solutions (Fig. 9). Owing to the limited solubility of this salt it was necessary to work at a higher temperature (60° C.).

A sharp contrast is at once apparent between the form of the two sets of curves (Figs. 8 and 9).

For small concentrations of NaCl (up to about .03

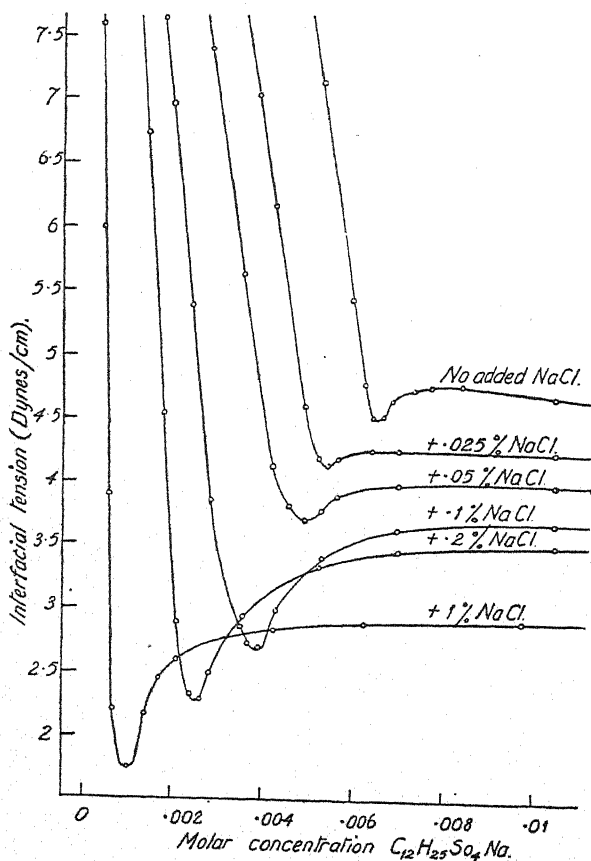


FIG. 8.—Influence of NaCl on interfacial tension of sodium dodecyl sulphate solutions at 20° C.

per cent.) the behaviour of the C_{18} salt is similar to that of the C_{12} salt, but at higher NaCl concentrations the minima which are associated with critical concentrations tend to disappear completely. Thus, while the behaviour in the micellar region is comparable in the two cases, the addition of NaCl to dilute solutions of octadecyl sulphate at first produces a relatively small lowering of interfacial tension, and further NaCl addition actually brings about an increase in tension. All solutions tested were quite clear even on standing at 60° C. for a considerable time, so that these observed increases in tension cannot be due to a salting-out of surface active material.

Since the change in behaviour could not be definitely attributed to the

difference in chain length, owing to the different temperatures involved, it was necessary to determine whether the effect produced by NaCl on the dodecyl salt was independent of temperature. Interfacial tension curves were therefore obtained in the presence of 0.075 per cent. NaCl over the temperature range 20°–80° C. (Fig. 10). These curves are of essentially the same form as those obtained for the C_{12} salt alone,²⁵ except that there is a general displacement towards lower concentrations. It is of interest to note that the temperature coefficient of critical concentration in the presence of 0.075 per cent. NaCl is almost identical with that obtained in the absence of added salt. It seems probable, therefore, that the difference in behaviour between the C_{12} and C_{18} salts in presence of NaCl can be attributed to difference in chain length. Since a lowering of critical concentration takes place, the salt effect on interfacial tension must be attributed partly to changes in the nature of the bulk solution. It was anticipated that a similar effect on surface tension might occur. Surface tension data obtained for the C_{12} salt in the presence of NaCl (Fig. 11) show that although the addition of NaCl produces little change in the minimum surface tension values, the depression of critical concentration is in agreement with that determined from interfacial tension measurements.

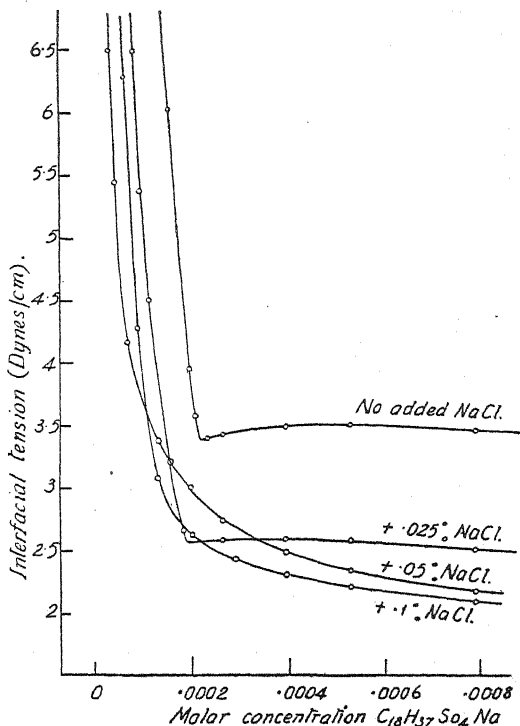


FIG. 9.—Influence of NaCl on interfacial tensions of sodium octadecyl sulphate solutions at 60° C.

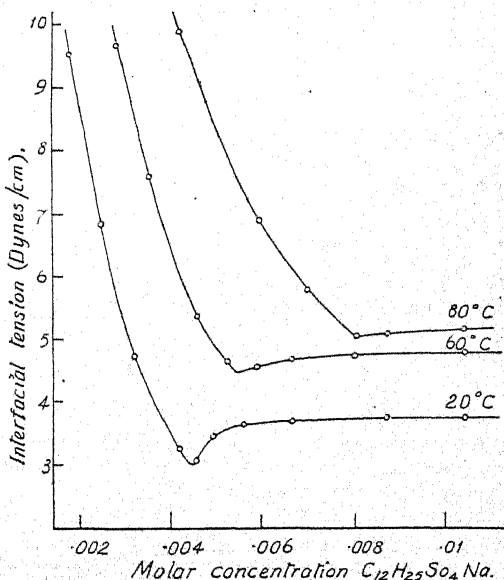


FIG. 10.—Interfacial tensions of sodium dodecyl sulphate solutions containing 0.75 per cent. NaCl, at various temperatures.

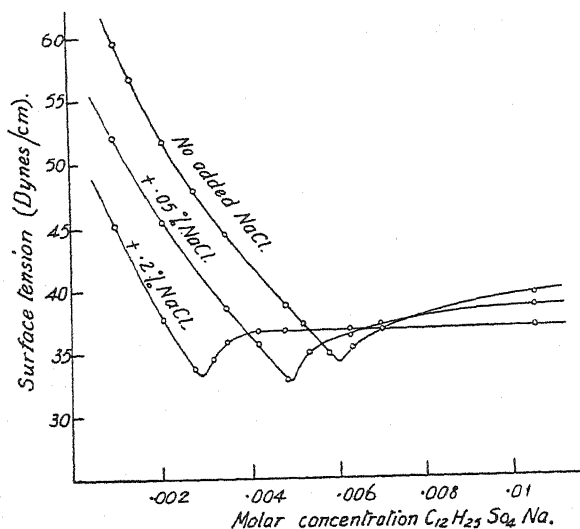


FIG. 11.—Influence of NaCl on surface tension of sodium dodecyl sulphate solutions at 20° C.

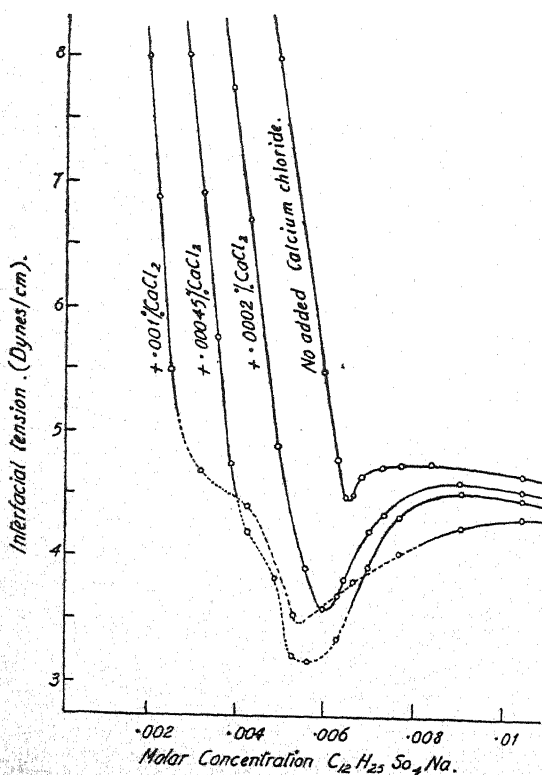


FIG. 12.—Influence of CaCl_2 on interfacial tension of sodium dodecyl sulphate solutions at 20° C.

Influence of Added Calcium Salts.

Experiments have been carried out in order to determine the influence of added divalent cations on surface activity. Interfacial tension curves for sodium dodecyl sulphate at 20° C. in the presence of various amounts of CaCl_2 are shown in Fig. 12. The dotted sections of the curves indicate regions of turbidity. By comparing the relative molar concentrations of NaCl and CaCl_2 required to produce a given lowering of tension, it is apparent that there is a considerable valency effect. In micellar solutions the ratio is about 40 : 1, which is of the same order as that given in the Hardy-Schultze Law for the coagulation of colloid systems. In concentrations below the critical, however, the quantity of NaCl necessary to produce a given lowering of tension is about 200 times greater than the corresponding amount of CaCl_2 required. Thus in a 0.002 M solution of sodium dodecyl sulphate, a lowering of 10 dynes/cm. in interfacial tension requires the presence of 10 molecules of NaCl for every long-chain ion, whilst the same lowering can be

brought about by the addition of one CaCl_2 molecule for every 20 long chain ions.

The general effect produced by added salts on interfacial tension is reflected in the surface tension data also obtained. The influence of CaCl_2 on the surface tensions of sodium dodecyl sulphate solutions at 20°C . has been studied (Fig. 13). Similar curves have been obtained for the tetradecyl sulphate (Fig. 14). In the latter case it was necessary to use a higher temperature (60°C .) in order to obtain complete curves, since at 30°C . turbidity occurred even with the smallest additions of CaCl_2 . In dilute non-micellar solutions of both of these compounds the ratio of the amounts of sodium and calcium salts required to bring about any given lowering of surface tension

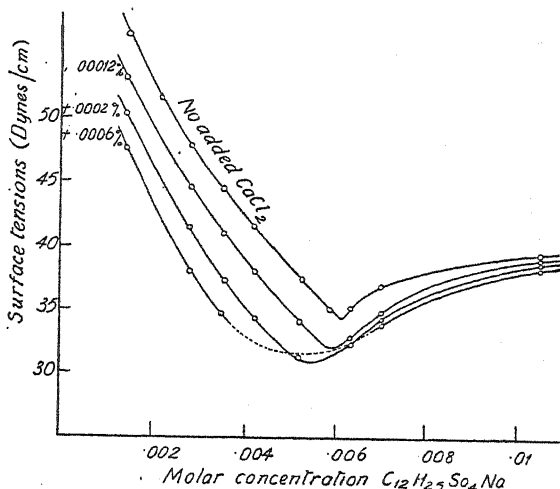


FIG. 13.—Influence of CaCl_2 on surface tension of sodium dodecyl sulphate solutions at 20°C .

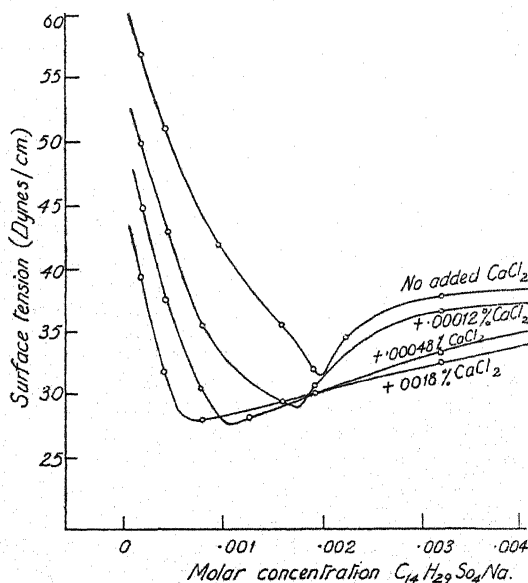


FIG. 14.—Influence of CaCl_2 on surface tension of sodium tetradecyl sulphate solutions at 60°C .

is of the same order (i.e. about 200:1) as that found from interfacial tensions. In the micellar region the relative effects of sodium and calcium become less marked. It is clear that in the non-micellar region the valency effect is highly specific, and may possibly be attributed to profound changes in the electrical conditions at the interface, rather than to any considerable influence on the bulk state. Nevertheless, the presence of very small quantities of calcium salt can displace the equilibrium between micelles and single ions to a marked degree. Thus for sodium tetradecyl sulphate solutions (Fig. 14) the critical micelle concentration is depressed to one third of its normal value by the addition of 0.0018 per cent. CaCl_2 (1 per cent = 0.09 M CaCl_2).

It is generally considered that compounds of this type are stable towards calcium salts. In these experiments clear solutions of sodium dodecyl sulphate were obtained at 20° C. in the presence of quite large amounts of calcium chloride, provided that the concentration of the dodecyl sulphate was sufficient to give rise to a micellar solution. If, however, the solutions were diluted to below the critical concentration, precipitation of calcium salt immediately occurred. Hence, although the calcium long-chain salt is relatively insoluble at 20° C., it is capable of assuming an anomalous solubility in the presence of colloidal aggregates formed either by higher concentrations of the sodium long-chain salt, or by increasing the temperature until the solubility of the calcium salt reaches the critical concentration.

This instability with respect to added calcium salts increases with increasing chain length. During an investigation of the effect of CaCl_2 on the surface tension of a non-micellar (0.00006 M) sodium octadecyl sulphate solution, at 60° C., it was found that not more than 5×10^{-6} per cent. CaCl_2 could be added without the formation of a visible turbidity. Appreciable changes in surface tension values were observed on the addition of as little as 5×10^{-7} per cent. CaCl_2 . It was difficult to obtain reproducible results for such low concentrations, since the amounts of stray contamination and impurities already present in the water ($K_{18} = 1-1.5 \times 10^{-6} \text{ ohms}^{-1} \text{ cm.}^{-1}$) were probably comparable with the concentrations of calcium chloride added.

The Effect of Various Other Added Salts.

Additional experiments were made to determine the influence of certain other salts on surface and interfacial tensions. In the case of iron and aluminium salts, the valency effect was obscured owing to the formation of colloidal hydroxides, and neither salt was found to be as efficient as calcium in lowering surface tension. The first addition of up to about 0.0008 per cent. of $\text{Al}_2(\text{SO}_4)_3$ to a 0.0004 M solution of sodium tetradecyl sulphate at 60° C. caused a slight increase in the tension, accompanied by a faint cloudiness. This initial increase in surface tension may possibly be attributed to the adsorption of surface active material on to the surface of the colloidal $\text{Al}(\text{OH})_3$ particles formed by hydrolysis. In this region the surface appeared to be semi-rigid. On increasing the concentration of $\text{Al}_2(\text{SO}_4)_3$ up to 0.0012 per cent. the solution cleared slightly, the surface became less rigid, and a sudden fall in the tension occurred to a value comparable to that found on the addition of calcium chloride.

It has been shown that in general the salt effect is independent of the nature of the anion. This is true for simple salts, but any tendency for the formation of a complex anion is at once reflected in the efficiency of the salt in lowering tension. Conversely, by comparing the quantities of a simple and a complex salt required to bring about a certain lowering of tension, it is possible to estimate the number of cations bound in the complex. This is clearly illustrated by some results obtained for sodium hexametaphosphate ($\text{NaPO}_3)_6$. Using a fixed concentration of sodium dodecyl sulphate, the concentrations of NaCl and sodium hexametaphosphate ("Calgon") necessary to produce any given lowering of tension were compared. In each case it was observed that the molar concentration of the hexametaphosphate (reckoned as NaPO_3) required was almost exactly twice the molar concentration of NaCl required. Considering the sodium hexametaphosphate molecule to have the empirical formula $(\text{NaPO}_3)_6$, it is evident from the above that only three of the six sodium atoms are free to ionise, the remaining three being bound into the complex anion. This indicates that sodium hexametaphosphate probably exists in solution as $\text{Na}_3(\text{Na}_3(\text{PO}_3)_6)$. An interesting effect was noted when sodium hexametaphosphate was added to a sodium dodecyl sulphate solution whose interfacial tension had already been lowered by the addition of calcium chloride. Progressive small additions of the hexametaphosphate increased the tension again to the value found for the alkyl sulphate solu-

tion in the absence of calcium chloride. Evidence is thus obtained that all the calcium is completely bound within the anionic complex, and is no longer capable of exerting divalent cation effect. Though the quantity of hexametaphosphate required for this purpose was so small as to have a negligible sodium effect, it is evident that the addition of amounts in considerable excess of that required to bind the calcium would cause the interfacial tension to fall again.

It may be mentioned here that some experiments which have been carried out show that the effect of added salts on the surface activity of paraffin-chain compounds giving surface active cations is dependent upon the valency of the added anions, in agreement with the suggestion recently made by Robinson.¹⁵ Interfacial tension data which have been obtained for dodecyl pyridinium chloride indicate that the sulphate ion produces a much greater lowering than does the chloride ion.

General Discussion.

Whilst it is not possible at this stage to advance any quantitative explanation of the change in surface activity on addition of salts, certain deductions of a somewhat tentative nature can be made.

It is clear from the observed depression of critical concentration produced by added salts, that micelle formation is facilitated by the presence of an excess of ions of opposite charge to the paraffin-chain ions. This is a natural consequence of the reduced repulsion between the polar groups of the aggregating ions. This reduction of effective charge may also be expected to influence surface activity. Although the decrease in mutual repulsion between the long-chain ions already adsorbed in the surface will bring about some reduction of surface pressure (and consequently an increase in surface tension), it will at the same time facilitate the migration of further surface active ions into the surface film. Since in nearly all cases the resultant effect of salt addition is a considerable lowering of tension, it would appear that the latter factor is predominant, particularly in the case of the shorter chain lengths. It may be recalled here that the interfacial tension data for the C_{18} salt (Fig. 8) showed at first a slight decrease, followed by an actual increase in tension with progressive salt additions. This may possibly be attributed to the fact that by virtue of the longer chain length, the adsorption is already high. The effect of added NaCl on the longer chain salts is manifest therefore in a lowering of the mutual repulsion in the existing adsorbed film, rather than in effecting there a further concentration of surface active ions.

In addition to the purely electrical effects described, the addition of salts will produce changes in the osmotic equilibrium in the region of the interface. The repulsion between the aqueous medium and the hydrophobic part of the paraffin-chain molecule, which results in a migration of the latter to the phase boundary, may be regarded as a restricting influence acting on the paraffin-chain ions to set up a Donnan Membrane Equilibrium. On addition of excess of the common small ion, the distribution of solute across some arbitrary bounding surface only a few molecular radii from the actual interface will be altered, and the apparent osmotic pressure operating to set an upper limit to the possible amount of adsorbed material will be considerably reduced.

Summary.

The effect of various added salts on the surface and interfacial tensions of long-chain alkyl sodium sulphates has been studied. It is shown that

the surface activity and the critical concentration for micelles are modified to an extent which is dependent upon the valency of the added cation, and independent of the nature of the associated anion. The magnitude of these effects is also governed by chain length and temperature.

The mechanism whereby surface activity is influenced by added electrolytes is discussed.

The authors are indebted to the Director of Research for his valuable advice and criticism, and to the Council of the British Launderers' Research Association for permission to publish this work.

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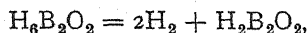
ON CERTAIN ISOMERIC COMPOUNDS OF BORON, HYDROGEN AND OXYGEN.

BY PROFESSOR RAMES C. RAY.

Received 18th March, 1937.

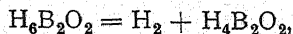
(Communicated by PROFESSOR TRAVERS.)

Some years ago Travers, Ray and Gupta¹ obtained a compound, now described as $\alpha\text{-H}_6\text{B}_2\text{O}_2$, in solution by heating a mixture of anhydrous boric oxide with magnesium powder in an iron vessel in a current of hydrogen, so that it deflagrated, and treating the product with water. Later, Ray² isolated the di-potassium salt of this compound. On adding acid to the solution of the α -compound, or of its salts, hydrogen was evolved according to the equation,



and on treating the acid solution with iodine, or on evaporating the acid solution and heating the residue gently, a dioxide, B_2O_2 , was obtained. It may be noted that this oxide is a very stable compound.¹ It is neither oxidised in solution by iodine, nor when it is mixed with excess of lime and water, the liquid evaporated to dryness, and the residue ignited strongly in a platinum crucible in air.

Travers, Ray and Gupta¹ found that when the mixture of boric oxide and magnesium did not deflagrate on heating, the B_2O_3 was not completely decomposed; and when the product was treated with water a solution was obtained which contained free boric acid and magnesium metaborate. They also found evidence that it contained a compound, apparently isomeric with $\alpha\text{-H}_6\text{B}_2\text{O}_2$, but differing from it in that it yielded one molecule of hydrogen only on treatment of the solution with acid, thus



the remaining hydrogen being removable on treatment with iodine, as

¹ *Some Compounds of Boron, Oxygen, and Hydrogen*, H. K. Lewis & Co. Ltd., 1916.

² *J. Chem. Soc.*, 1922, 1088.

in the case of the α -compound, to produce the oxide B_2O_3 . The compound, which was probably present as a magnesium salt, was unstable, and on standing, particularly in the presence of strong ammonia, changed into the α -compound. The di- and tetra-potassium salts of this compound, the β - $H_6B_2O_2$, have now been isolated, and the method of preparation and properties are described in this paper.

In preparing the derivatives of β - $B_2H_6O_2$, an intimate mixture of 1 part by weight of fused boric oxide and 2.2 parts of magnesium powder, carefully dried, was heated in an iron tube in a current of hydrogen. Instead of carrying out the operation so that the reaction was incomplete, however, the tube was heated strongly, so that the mixture deflagrated, and then, to the powdered product, about 2 per cent. of magnesium powder and 15 per cent. boric acid was added. This mixture was then treated with N/100 potassium hydroxide solution in a vessel cooled with ice. Hydrogen containing traces of boron hydrides was evolved. When the reaction was complete the solution was filtered, and evaporated *in vacuo* at the ordinary temperature. The first and last fractions were rejected; the middle fractions from five or six different preparations were collected, dissolved in

TABLE I.

α - $B_2H_4K_2O_2$	Found K	56.96, 57.16, 57.42; calcd.	57.35.
	" B	16.05, 15.95, 16.10; "	16.18
	Ratio H/I	2.04, 1.96, 2.00.	
β - $B_2H_4K_2O_2$	Found K	57.45, 57.40, 56.95; calcd.	57.35
	" B	15.88, 15.98, 16.11; "	16.18
	Ratio H/I	0.49, 0.50, 0.50;	
β - $B_2H_2K_4O_2$	Found K	73.72, 73.61, 73.60; calcd.	73.59.
	" B	10.40, 10.36, 10.29; "	10.37.
	Ratio H/I	0.50.	
β - $B_2H_2K_2O_2$	Found K	58.32, 58.28, 57.97; calcd.	58.22.
	" B	16.32, 16.38, 16.40; "	16.41.
	No hydrogen with acid.		

carbon dioxide-free water containing a little boric acid, and subjected to fractional crystallisation. By repeating this process several times two compounds were separated, one of which appears to be the di-potassium salt of the compound, β - $B_2H_6O_2$, which is isomeric with α - $B_2H_6O_2$ —it will therefore be referred to as β - $B_2H_4K_2O_2$, and the other is a di-potassium salt which will be referred to as β - $B_2H_2K_2O_2$. It is a salt of the compound β - $B_2H_4O_2$.

If the mixture of magnesium boride with added magnesium and boric acid is treated with water in a vessel cooled with ice, and N/20 potassium hydroxide solution is added to the filtered solution, magnesium metaborate and magnesium hydroxide are precipitated. This is filtered off, and the solution is shaken for two days in an exhausted apparatus, when a further quantity separates. The filtered solution on fractional crystallisation then yields a compound which appears to be a tetra-potassium derivative of β - $B_2H_6O_2$, having the formula β - $B_2H_2K_4O_2$. It has also been found that the β -di-potassium salt is readily converted into β -tetra-potassium salt when a weighed quantity of the former is dissolved in conductivity water and treated with the requisite quantity of dilute potassium hydroxide solution. The tetra-potassium compound may be obtained by evaporating the solution *in vacuo*.

All the compounds form colourless and well-defined crystals, and do not contain water. They all act as powerful reducing agents. Salts of silver, gold, etc., are reduced to metals, and with copper sulphate solutions a red precipitate of "copper hydride" is obtained. Both α - and β - $B_2H_4K_2O_2$ give with nickel sulphate a greenish precipitate which contains both nickel and boron. The salts with the exception of β - $B_2H_4K_2O_2$ are

fairly stable when preserved in a vacuum or in a vessel free from moisture and carbon dioxide. They are all completely oxidised by nitric acid.

The analysis of the compounds was carried out in the manner described in the previous paper.² The results obtained are set down in Table I., which includes the data obtained for $\alpha\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$, for comparison.

TABLE II.

Wt. of Salt.	Gram Mols. Salt.	C.c.s Hydrogen at N.T.P.	C.c.s N/10 Iodine Soln. Absorbed.	Gram-equivs. Hydrogen.	Gram-equivs. Iodine.	H/I.
$\beta\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$.						
0.1436	0.00105	23.4	43.2	0.00211	0.00432	0.49
0.1152	0.00086	18.8	33.5	0.00169	0.00335	0.50
0.0976	0.00072	15.8	28.6	0.00142	0.00286	0.50
$\beta\text{-B}_2\text{H}_2\text{K}_4\text{O}_2$.						
0.1272	0.00060	13.8	24.4	0.00123	0.00244	0.50
$\beta\text{-B}_2\text{H}_2\text{K}_2\text{O}_2$.						
0.1336	0.00100	nil	39.6	nil	0.00396	nil

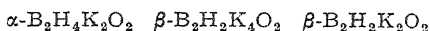
Table II. shows the results obtained by treating $\beta\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$ and $\beta\text{-B}_2\text{H}_2\text{K}_4\text{O}_2$ with acid, pumping off the hydrogen, adding excess of N/10 iodine solution to the acid liquid, and allowing it to remain for 3 hours in the dark. The equivalent conductivities of solution of the compounds, measured at 25°, are given in Table III.

TABLE III.

$\alpha\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$.								
ν	.	32	64	128	256	512	1024	∞
Λ	.	124.4	133.2	138.8	142.9	146.9	148.5	154.0
α	.	0.81	0.86	0.90	0.93	0.95	0.96	π
$\beta\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$.								
ν	.	32	64	128	256	512	1024	∞
Λ	.	267.0	295.6	320.0	344.5	360.8	377.4	410.0
α	.	0.65	0.72	0.78	0.84	0.88	0.92	π
$\beta\text{-B}_2\text{H}_2\text{K}_4\text{O}_2$.								
ν	.	32	64	128	256	512	1024	∞
Λ	.	96.1	105.4	116.3	128.8	134.9	143.4	155.0
α	.	0.62	0.68	0.75	0.83	0.87	0.92	π
$\beta\text{-B}_2\text{H}_2\text{K}_2\text{O}_2$.								
ν	.	32	64	128	256	512	1024	∞
Λ	.	136.7	144.9	150.7	157.4	159.6	162.8	170.0
α	.	0.80	0.85	0.89	0.93	0.94	0.96	π

The difference between Λ_∞ for $\beta\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$ and $\beta\text{-B}_2\text{H}_2\text{K}_4\text{O}_2$ is 255, which is close to 275.5, the difference between the values of Λ_∞ for acetic acid and potassium acetate at 25°, and about the value to be expected if the former is the acid salt corresponding to the latter. The values of the

differences $A_{1024} - A_{32}$ for the three normal salts approximate to the value of the product $11n$, where n is the basicity of the acid^{3, 4, 5}.



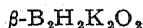
$A_{1024} - A_{32}$	22.4	44.8	26.7
$n \times 11$	22	44	22

Travers, Ray and Gupta¹ determined the molecular weight of the ammonium salt of the $\alpha\text{-B}_2\text{H}_4\text{O}_2$ by the freezing-point method, and allow for the dissociation found a value for n in the formula $(\text{BH}_3\text{O})_n$ between 1.8 and 2.2. Table IV. shows the results of experiments with the three new compounds.

Without assuming any direct physical connection between the numerical value of α , and that of the activity coefficient γ , since the two are generally closely related, the value of the latter being about 10 per cent. lower than that of the former, the data in Table III. may be used to obtain an estimate of the molecular weights of the compounds, on the alternative assumptions that the molecules contain one or two atoms of boron. The calculations on the basis of the former assumption for the compounds



and



are given in Table V.

Calculations based upon the supposition that the molecules $\beta\text{-B}_2\text{H}_4\text{O}_2$ and $\beta\text{-B}_2\text{H}_2\text{O}_2$ would dissociate into $(1 + 2)$ and $(1 + 1)$ ions respectively lead

to values 43 and 35 respectively from the data from the first experiment (a) in each case. The decision as to the complexity of the compound $\beta\text{-B}_2\text{H}_4\text{K}_4\text{O}_2$, which is evidently an acid salt corresponding to the compound $\beta\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$, and is very unstable, must rest mainly on its relation to the latter compound. However, considering the whole of the data, there seems to be no doubt but that these molecules contain two atoms of boron.

The properties of the compounds which have been described are very

TABLE IV.

	Wt. of Substance Dissolved in 100 Gms. of Water. <i>w.</i>	Depression of Freezing Pt. <i>d.</i>	Molecular Wt. <i>M.</i>
$\beta\text{-B}_2\text{H}_4\text{K}_2\text{O}_2$	(a) 0.1029 (b) 0.0772 (c) 0.0617	0.058° 0.044° 0.035°	33.0 32.6 32.4
$\beta\text{-B}_2\text{H}_2\text{K}_4\text{O}_2$	(a) 0.1237 (b) 0.2562 (c) 0.3728	0.042° 0.078° 0.108°	54.8 61.1 64.2
$\beta\text{-B}_2\text{H}_2\text{K}_2\text{O}_2$	(a) 0.1025 (b) 0.1156 (c) 0.1546	0.038° 0.042° 0.055°	50.0 51.2 52.2

TABLE V.

Experiment.	(a).	(b).	(c).
$\beta\text{-B}_2\text{H}_2\text{K}_4\text{O}_2$ (No. of ions = $1 + 4 = 5$).			
<i>v</i> . . .	86	41	28
α . . .	0.72	0.64	0.61
<i>M</i> calc. .	54.6-62.4	58.8-66.3	61.6-70.7
<i>M</i> found .	54.8	56.1	64.2
$\beta\text{-B}_2\text{H}_2\text{K}_2\text{O}_2$ (No. of ions = $1 + 2 = 3$).			
<i>v</i> . . .	65	56	43
α . . .	0.85	0.84	0.83
<i>M</i> calc. .	48.6-53.6	50.0-53.6	50.4-53.6
<i>M</i> found .	50.0	51.2	52.0

³ Ostwald, *Z. physikal. Chem.*, 1887, 1, 74.

⁴ Walden, *ibid.*, 1887, 1, 529; 1888, 2, 49.

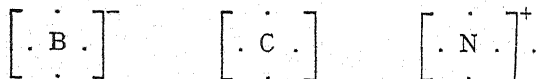
⁵ Bredig, *ibid.*, 1893, 12, 230.

sharply defined, and the stoichiometric relations in the reactions in which they take part are so simple that there can be no doubt whatsoever as to the facts. These appear to be sufficiently numerous and definite to justify an attempt to assign structural formulæ to the compounds, though we have to assume a somewhat different outlook than when dealing with carbon compounds.

It may be assumed that the borohydrates which we are discussing are closely related to diborane, B_2H_6 . The constitution of that hydroboron has been discussed at very considerable length in papers published recently, particularly by Pauling,⁶ G. N. Lewis,⁷ R. S. Mulliken,⁸ Stock, Wiberg and Mathing,⁹ and Wiberg.¹⁰ Briefly, it may be stated that the majority of these authors stress the similarity of diborane and ethane, the hydrogen atoms being held by a system in which the strength of the B—H bond is uniformly equivalent to 5/6 of that of an electron pair. The B—B bond is somewhat stronger than the B—H bond, and equivalent to a normal electron pair between boron atoms in an otherwise uniform field, and weaker than a normal C—C bond.

Wiberg¹⁰ discusses the constitution of the hydroborons at very considerable length, and he divides them into two classes, with only one of which, containing the compounds B_2H_6 and B_4H_{10} are we concerned, and with the second of these only to mention the fact that it is probably the parent of the borohydrate $B_4H_{10}O_4$ discovered by Travers, Ray and Gupta¹ in 1913. Wiberg¹⁰ and his associates call attention to the analogies between diborane and ethylene. The observed value of the parachor was found to be 121.9, which agrees with the calculated value, 121.2, made up of the values for two B atoms (2×16.4), four H atoms (4×17.1) one double bond (23.2), and two electro-valencies (-2×1.6). The constitutional similarity between diborane and ethylene is also brought out by the fact (Hausser, unpublished¹⁰), that the ultra-violet absorption spectra of both compounds show bands in the region 185-210 $\mu\mu$, where none are observed in the case of ethane.

The analogous behaviour of diborane and ethylene points to a similarity in their electronic structures, and this idea may be extended to show that the hydroborons and borohydrates are by no means unique. Diborane itself, and the compounds $B_6H_{12}O_6$ yield stable ions, of which the electronic structure must be similar to that of the $(BF_4)^-$ ion, and also to the stable compounds containing the structures,



The notation is doubtless entirely conventional, but that there is a connection between the structures is clear. In writing the formula for diborane $[B_2H_4]-H_2^{++}$ it is not implied that any particular hydrogen atoms are differentiated from the others, though the compound forms salts.

One explanation of the existence of isomers is that, as in the case of carbon compounds, the double bond implies inability of the doubly bonded boron atoms to rotate. If, then, we are content to represent the α - and β - $H_6B_2O_2$ by the formulæ,

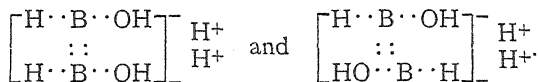
⁶ *J.A.C.S.*, 1931, **53**, 3225.

⁸ *Ibid.*, 1935, **57**, 635.

⁷ *J. Chem. Physics.*, 1933, **1**, 17.

⁹ *Ber.*, 1936, **69**, 2811.

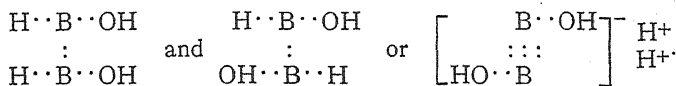
¹⁰ *Ibid.*, 2816.



without considering their constitution in further detail, we can see that the α -compound might be able to lose two atoms of hydrogen more readily than the β -compound. It is easy to assign a formula,



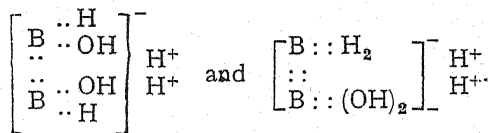
to the product from the α - $\text{H}_6\text{B}_2\text{O}_2$. In the case of the β -compound, however, there are alternatives, which may be represented by



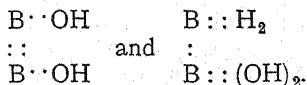
The first two formulæ are identical, and represent the same compound, as the B : B bond is now eliminated. This formula, and that written above to represent the derivative of the α -compound, include the electronic arrangement $\cdot \dot{\text{B}} \cdot$, indicating that the change in electronic arrangement is the same in either case, though the α -compound loses two more atoms of hydrogen than the β -compound. The alternative formula, which represents the setting up of a B \equiv B linkage, and no change in the electronic structure, has nothing in its favour.

It is probable that the compound, of which the potassium salt $\text{H}_2\text{B}_2\text{O}_2\text{K}_2$ was obtained in the process of preparing β - $\text{H}_6\text{B}_2\text{O}_2$, is identical with that obtained by adding acid to the β - $\text{H}_6\text{B}_2\text{O}_2$ or its salts, as neither compound, in presence of acid, loses hydrogen. It must be observed, however, that it should also be derived from α - $\text{H}_6\text{B}_2\text{O}_2$ by the elimination of two atoms of hydrogen; but even if it is not possible to effect this change directly, it does not mean that the connection does not exist.

It is also possible to represent the relationship between the α - and β - $\text{H}_6\text{B}_2\text{O}_2$ by assigning to them the formulæ,



The products of the action of acid on them may now be represented by



Here again the process involves a change in electronic structure from $\cdot \dot{\text{B}} \cdot$ to $\cdot \dot{\text{B}} \cdot$ in each case. As the stability under different circumstances appears to depend mainly upon electronic structure, the process appears to be equally well represented by either of the two systems. However, as the work of Travers, Ray and Gupta suggests that the β - $\text{H}_6\text{B}_2\text{O}_2$ does seem to undergo change into the α - $\text{H}_6\text{B}_2\text{O}_2$, it seems to be likely that the cis- and cis-trans formulæ are the more probable.

It is quite clear that the structural formulæ which represent space relationships so well in the case of the carbon compounds, though less effectively in the case of nitrogen compounds, may be used in the case of boron compounds only to indicate the general character of certain chemical processes. Indeed, much of the theoretical work, to which brief reference has been made, points to their limitations. It is also clear that we have in these cases to focus our attention particularly on changes in electronic arrangement, rather than on the apparent bonding of the atoms.

It would serve no useful purpose to discuss further the relationship between the constitution of the ions of the salts in the solutions, and of the unionised compounds, which, if they exist, are generally unstable. The mechanism of the elimination of hydrogen is also a matter which may be left for future discussion; but the study of it may throw light on the mechanism of dissociation of ethane, and ethylene, to which the process is doubtless related.

In conclusion I have to thank Professor M. W. Travers for helpful discussion continued over a number of years, and in particular in connection with the preparation of the present paper.

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KINETICS OF THE SOLVENT DECOMPOSITION OF NITRAMID IN H_2O-D_2O MIXTURES.*

BY VICTOR K. LA MER AND JOSEPH GREENSPAN.

Received 5th July, 1937.

The concepts of rate of transfer of protons,¹ the concentration of intermediate complexes,² "spontaneous" rearrangement,³ as well as various combinations of these concepts, have from time to time been advanced as mechanisms to explain the kinetics of protropic reactions. Deuterium oxide and its mixtures with protium oxide have already proven valuable as solvents for the investigation of such reactions, because they permit a more direct examination of the mechanism than has hitherto been possible.^{4, 5}

* Contribution from the Department of Chemistry, Columbia University.

¹ (a) Brönsted and Kai Pedersen, *Z. physik. Chem.*, 1924, 108, 185; (b) Brönsted, *Chem. Rev.*, 1928, 5, 231.

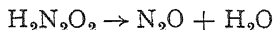
² (a) Bjerrum, *Z. physik. Chem.*, 1924, 108, 82. (b) The recent theory of Eyring, *J. Chem. Physics*, 1935, 3, 107 *et seq.*, on the absolute rate of reactions gives quantum mechanical dress to this proposal and in the limited case of very simple gaseous reactions, permits of statistical mechanical calculation of the concentration of the "complex." Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, 3, 492, treat reactions in condensed phases.

³ For example, keto-enol tautomerism, consult the Symposium on "Kinetics of Reactions," *Chem. Rev.*, 1935, 17, 43 *et seq.*, for further elaboration of this and other proposals.

⁴ Hamill and La Mer, *J. Chem. Physics.*, 1934, 2, 891; 1936, 4, 144, 294 and 395.

⁵ Wynne-Jones, *Chem. Rev.*, 1935, 17, 115.

In this laboratory we have taken the view that precision measurements were essential if distinctions were to be drawn between proposed mechanisms. A series of conductimetric,⁶ electrometric,⁷ and kinetic⁴ measurements of proto- and deuterotropic processes and related equilibria has accordingly been undertaken. In this research the preliminary measurements of Marlies and La Mer⁸ on the rate-depressing effect of 5 per cent. additions of D₂O on the solvent decomposition of nitramid in 0.01 molal hydrochloric acid:



are extended to the entire range of H₂O—D₂O mixtures. The important role that nitramid decomposition has played in the development of the modern concepts of acid-base catalysis, its remarkable obedience⁸ to a first order rate equation, and its freedom from complicating side reactions—an ideal behaviour which we now find to be equally true in H₂O—D₂O mixtures—make investigations of this reaction particularly significant. Furthermore, in spite of much careful work, the exact nature of the decomposition is still uncertain.^{8, 9}

Experimental.

The apparatus, described in detail elsewhere,¹⁰ was of semi-micro proportions and was designed to employ only 10 ml. of solution. The results equal in precision those secured by a similar technique with the macro apparatus requiring 200 ml.⁸ The solutions containing the nitramid were shaken and pumped (Hyvac) for one half hour before readings were taken, to ensure complete displacement of air from the solutions by the evolved N₂O.

Nitramid was prepared according to the improved method of Marlies and La Mer,¹¹ whereby the yield in the last step has been increased to 80 per cent. or better.

Deuterium Oxide. All samples were subjected to at least three purification steps: atmospheric pressure distillation from alkaline permanganate (for 50 to 100 c.c. of solvent one pellet NaOH and a few crystals of KMnO₄); followed by atmospheric pressure distillation from acid dichromate (a few crystals CrO₃ and one drop of H₃PO₄). The last stage involved a very slow vacuum distillation in Pyrex glass. After all dissolved gas had been removed by freezing and pumping, the apparatus was sealed; the receiver was surrounded by a solid CO₂-ethyl alcohol bath, while the distilling side was kept at 25°-40° C. The distillate collects slowly in the form of a snow. The specific conductance is less than 10⁻⁶ mhos. The densities of the waters were determined in 10 ml. pycnometers, weighed to 0.1 mg.

Hydrochloric Acid Solutions. Definite weights of constant boiling acid were added to known weights of heavy water yielding solutions approximately 0.008 to 0.01 molal.

Precision of Measurements. Duplicate experiments on two separate samples of each H₂O—D₂O mixture were always run simultaneously, the duplicates agreeing in the value of *k* from 0.1 per cent. to a maximum of 2 per cent. (average of 1 per cent.), depending on the solutions used. The rate constants, *k*, were calculated in all cases, except for pure H₂O,

⁶ Baker and La Mer, *J. Chem. Physics*, 1935, **3**, 406; La Mer and Chittum, *J. Am. Chem. Soc.*, *in press*.

⁷ Korman and La Mer, *ibid.*, August, 1936.

⁸ Marlies and La Mer, *ibid.*, 1935, **57**, 1812.

⁹ Kai Pedersen, *J. Physic. Chem.*, 1934, **38**, 581.

¹⁰ Greenspan, La Mer and Liotta, *J. Am. Chem. Soc.* (*in press*).

¹¹ Marlies and La Mer, *J. Am. Chem. Soc.*, 1935, **57**, 2008. *Inorganic Synthesis* (*in press*).

by the Guggenheim¹² method, combined with the method, of least squares for equal intervals.¹³ The H₂O result listed represents the average constant of five independent series of measurements, calculated by the customary method in some cases and by the Guggenheim method in others. A typical experiment is given in the preceding paper.¹⁰ To facilitate direct comparison, the temperature employed ($28.84^\circ \pm 0.002^\circ \text{C.}$) was the same as that used by Marlies and La Mer.⁸

Experimental Results.

Table I summarizes the results obtained. In column 1 are found the *absolute densities* (gm./ml. at 25°) of the waters; column 2, $p = \Delta d/0.1079$ gives the corresponding atom fraction (multiplied by 0.99707) of deuterium in the solvent, assuming^{14, 15} a specific gravity (*S*) of 1.1079 (25°C.) for pure D₂O; column 3 contains the experimentally measured and averaged specific rate constants, 10⁶k meas. ($\log_{10} \text{min.}^{-1}$). Columns 4, 5 and 6 contain, respectively, the concentrations in moles-litre of H₂O, HDO and D₂O calculated by assuming the equilibrium:¹⁶

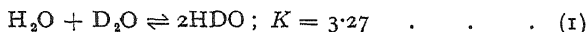


TABLE I.—SOLVENT DECOMPOSITION OF NITRAMID AT 24.84°C.

d_{25°	100p.	10 ⁶ k meas.	$m_{\text{H}_2\text{O}}$	m_{HDO}	$m_{\text{D}_2\text{O}}$	$m'_{\text{H}_2\text{O}}$	$m'_{\text{D}_2\text{O}}$
0.99707	0.00	1266.0	55.331	—†	—	55.331	—
1.00213	4.69	1176.0*	50.293	4.883	0.145	52.725	2.595
1.02739	28.10	861.1	29.091	21.381	4.806	39.746	15.534
1.04652	45.83	661.8	16.946	26.052	12.249	29.929	25.321
1.08113	77.91	384.4	3.047	18.349	33.792	12.191	42.999
1.10001	95.40	271.7	0.141	4.807	50.209	2.537	52.623
1.10354 (1.1046)	98.67 (100.00)	250.7 (243.0)	— —	1.446 —	53.694 (55.149)	0.733 —	54.417 (55.149)

* Determined with macro apparatus by Marlies and La Mer.⁸

† These calculations are made on the basis of complete absence of D in ordinary H₂O.

and solving the derived quadratic equation:

$$2x = 0.8055p - 247.848 \pm 61428.60 + 54276.01p - 54675.28p^2,$$

where

$$p = \Delta S/0.1079$$

$$2x = \text{concentration of HDO, m./l.}$$

$$55.15 p - x = \text{concentration of D}_2\text{O, m./l.}$$

$$(55.33 (1 - p)) - x = \text{concentration of H}_2\text{O, m./l.}$$

Columns 7 and 8, respectively, give the concentrations in moles/litre of H₂O and D₂O, but assume the absence of any HDO. Thus $m'_{\text{D}_2\text{O}} = pM$; $m'_{\text{H}_2\text{O}} = (1 - p)M$; *M* = moles of H₂O + D₂O per litre, being equal to $997.07/18.02 = 55.331$ moles/litre for pure H₂O at 25°C. , $1107.9 \times 0.99707/20.03 = 55.149$ moles/litre for pure D₂O.¹⁷

¹² Guggenheim, *Phil. Mag.*, 1926, (7), 2, 538.

¹³ Roeser, *Bur. Standards Bull.*, 1920, 16, 363 (Scientific paper 388); and ref. 8.

¹⁴ Lewis and Luten, *J. Am. Chem. Soc.*, 1933, 55, 5061.

¹⁵ Taylor and Selwood, *ibid.*, 1934, 56, 998.

¹⁶ (a) Topley and Eyring, *J. Chem. Physics*, 1934, 2, 217; (b) Farkas, *Light and Heavy Hydrogen*, pp. 180-181, Cambridge Press, 1935.

¹⁷ It is assumed throughout this discussion that the H₃O⁺ (D₃O⁺) ion (arising from the 0.01 molal HCl employed) exerts a very small and constant catalytic effect; this is plausible in view of the small catalytic and concentration effects⁸ of HCl in H₂O, and the low concentration employed here.

Discussion of Results.

One is confronted with several possibilities in selecting a mechanism for the decomposition of nitramid in H_2O — D_2O mixtures. The data, however, are sufficiently accurate to eliminate some of the possibilities. The simplest assumption, namely, that the added proto nitramid does not exchange with the solvent but decomposes at a slower rate on collision with a D_2O molecule than with an H_2O molecule may be dismissed, since this mechanism requires a linear decrease in velocity with the D content of the solvent. Actually the experimental curve exhibits

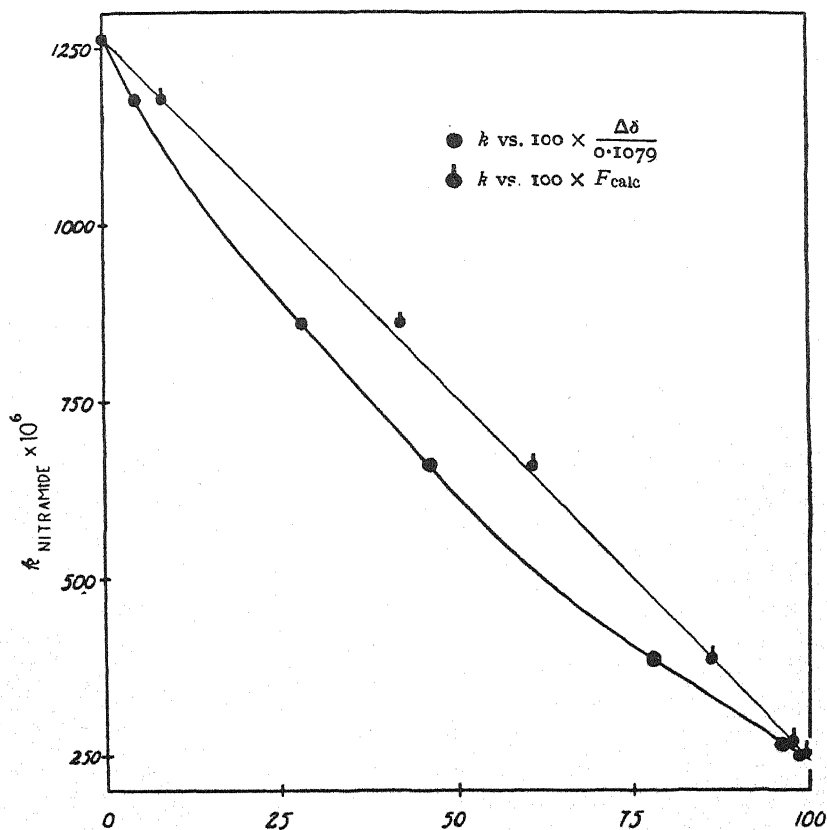


FIG. 1.

a marked sag characteristic of the reaction rates of other reactions⁴ (Fig. 1).

A related mechanism, extended to include the HDO formed by equilibrium 1, would take the form:

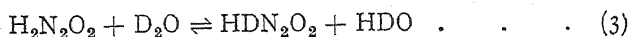
$$k_{\text{meas}} = k_{\text{H}_2\text{O}}m_{\text{H}_2\text{O}} + k_{\text{D}_2\text{O}}m_{\text{D}_2\text{O}} + k_{\text{HDO}}m_{\text{HDO}} \quad (2)$$

Substituting the measured value $0.001266/53.33 = 2.88 \cdot 10^{-5}$ for $k_{\text{H}_2\text{O}}$ and the slightly extrapolated value $0.0002430/55.15 = 4.406 \cdot 10^{-6}$ for $k_{\text{D}_2\text{O}}$ (see Table I.) eq. 2 may be solved for k_{HDO} . The results, column 3, Table III., show a rising constant, hence this mechanism is unlikely.

The protons in nitramid, as in other weak acids, undoubtedly undergo

rapid exchange with the deuterium of the solvent to yield an equilibrium mixture of deuterio- and proto-nitramid substrates. One can, in this manner, extend eq. 2 to include several additional terms involving cross products of the proto- and deuterio-nitramids with the three varieties of waters, but in the absence of an independently measured exchange constant for the $\text{H}_2\text{N}_2\text{O}_2\text{--D}_2\text{O}$ equilibrium, it is difficult to test such a complicated hypothesis at the present time. However, the complete absence of any observable drift of k_{meas} in mixtures of $\text{H}_2\text{O--D}_2\text{O}$ with progress of the reaction eliminates all mechanisms that involve a rate of attainment of an exchange equilibrium that is not exceedingly rapid compared to the rate-determining decomposition step.

Assume an equilibrium of the type



and that $V = k_{\text{meas}} - C_{\text{total nitramid}}$

$$= k'_D \cdot m_{\text{HDN}_2\text{O}_2} + k'_H \cdot m_{\text{H}_2\text{N}_2\text{O}_2} \quad (4)$$

or in its corresponding form

$$k_{\text{meas}} = k'_D \cdot F + k'_H \cdot (1 - F) \quad (5)$$

where

$$F = \frac{m_{\text{HDN}_2\text{O}_2}}{m_{\text{HDN}_2\text{O}} + m_{\text{H}_2\text{N}_2\text{O}_2}}$$

Here k'_D and k'_H represent the specific rates at which the deuterio- and proto-substrates decompose (243.6×10^{-6} and 1266×10^{-6}) in D_2O and in H_2O , the medium having *no direct kinetic* influence on the rate-determining step except by regulating the exchange equilibrium (3).

Equation (5) may be solved for F for each value of p and a value of $K_N = \frac{(\text{HDN}_2\text{O}_2)(\text{HDO})}{(\text{H}_2\text{N}_2\text{O}_2)(\text{D}_2\text{O})}$ calculated. The results given in column 3, Table II, give an excellent constant 3.27 ± 0.18 . If the calculation is

TABLE II.

p .	F .	K_N .	K'_N .	K''_N .
0.0469	0.0880	3.37 *	33.46 *	1.96 *
0.2810	0.3958	2.91	3.97	1.68
0.4583	0.5906	3.07	2.00	1.71
0.7791	0.8618	3.39	0.56	1.77
0.9540	0.9720	3.32	0.10	1.67
0.9867	0.9925	3.55	—	1.78
		3.267 ± 0.18		1.759 ± 0.075

* Determined by macro method, Marlies and La Mer.

reversed by using the average value of K_N , the calculated values of k agree with the measured values within the experimental error except for $p = 0.28$ and 0.45 (column 4, Table 3).

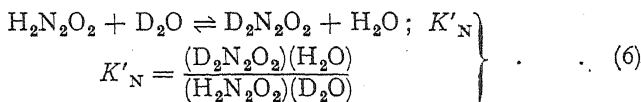
The striking result of this calculation is evident when k_{meas} is plotted against F , the fraction of deuterium in the substrate, instead of p , the

TABLE III.

p .	$10^6 k_{\text{meas.}}$	$10^7 k_{\text{HDO}}$	$10^6 k_N \text{ Calc.}$	$10^6 k'_N \text{ Calc.}$
0.0469	1176.0 *	51 *	1176.0	1184.0
0.2810	861.1	82	832.9	849.2
0.4583	661.8	84	646.4	654.1
0.7791	384.4	90	388.8	385.0
0.9540	271.7	98	272.2	270.3
0.9867	250.7	98	251.4	250.8

* Determined by macro method, Marlies and La Mer.⁸

fraction of deuterium in the solvent. The points now adhere closely to a straight line (Fig. 1). If we assume that two protons are exchanged



and proceed in similar manner, substituting $\frac{(\text{H}_2\text{O})}{(\text{D}_2\text{O})} = \frac{M_{\text{H}_2\text{O}}}{M_{\text{D}_2\text{O}}}$ of Table I,

we find that K''_N drifts violently (Table II.), which indicates that the exchange of one and not two protons in the exchange equilibrium is kinetically important. This result agrees with the mechanism suggested by Pedersen, that the proton bound to nitrogen in the "aci" form of nitramid, HNNOOH , is involved in the rate-determining step. Nitramid is a weak acid ($K = 10^{-7}$); it is reasonable to assume that this proton exchanges instantly, whereas the rate-determining step involves only the second proton (probably bound to nitrogen) which probably does not exchange as rapidly. It must be mentioned that if $M'_{\text{H}_2\text{O}}$ and $M'_{\text{D}_2\text{O}}$ (i.e., the stoichiometric concentrations neglecting the HDO equilibrium) are substituted in (6) a remarkably good constant K'_N is obtained, which reproduces the velocity constants exceedingly well. If any significance is to be ascribed to this agreement, it means that the neglect of the HDO equilibrium is compensated for by the neglect of the corresponding HDN_2O_2 equilibrium.

A mechanism of nitramid decomposition based essentially on the prototropic transfer as the rate-determining step has been proposed by Wynne-Jones.⁵ However, the value $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 20$ predicted from this mechanism is not in agreement with the experimentally determined ratio 5.21.

From this discussion it appears that the present data are insufficient, *per se*, to distinguish unequivocally between certain of the proposed mechanisms. An experimental test of some of these may be secured, however, through rate measurements¹⁸ on deuterio nitramid, $\text{D}_2\text{N}_2\text{O}_2$. Thus if both deuterons of $\text{D}_2\text{N}_2\text{O}_2$ are exchanged instantly, the rates of decomposition of both $\text{D}_2\text{N}_2\text{O}_2$ and $\text{H}_2\text{N}_2\text{O}_2$ in 100 per cent. H_2O should be equal; the decomposition rates of $\text{D}_2\text{N}_2\text{O}_2$ and of $\text{H}_2\text{N}_2\text{O}_2$ in 100 per cent. D_2O should likewise be equal to each other. Furthermore, the dependence of the decomposition rate of $\text{D}_2\text{N}_2\text{O}_2$ on p should coincide

¹⁸ The prototropic exchange method employed by Wynne-Jones (*J. Chem. Physics*, 1934, 2, 381) for obtaining heavy nitroethane is difficult here, since the nitramid molecule is unstable.

with that of $\text{H}_2\text{N}_2\text{O}_2$ on p . On the other hand, if only one proton, the "acidic" hydrogen, exchanges rapidly, then, in the mixed waters, HNNOOD and HNNOOH will be produced when proto nitramid is added, whereas DNNOOH and DNNOOD will be produced when deuterio nitramid is employed. If, then, the rate-determining step is the rate of transfer of the second proton (or deuteron), the rates of decomposition should be different for the proto and for the deuterio nitramids in the same concentration of heavy water mixtures. Experiments by Mr. Hochberg show that deuterio nitramid decomposes in light water at a rate 1255×10^{-6} . The investigation is being continued.

Summary and Conclusions.

1. The rates of the solvent decomposition of nitramid have been determined by a high precision semi-micro gas evolution method over the entire range of $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures.

2. The rate in 100 per cent. H_2O is 5.21 times faster than in 100 per cent. D_2O , when both are 0.01 molal in HCl .

3. A graph of the decomposition rate vs. atom fraction of deuterium in the solvent exhibits a sag curve characteristic of other prototropic reactions that have been studied.

4. The kinetic data can be interpreted on the basis of an exchange between the protons of the substrate and the deuterons of the solvent. Although the exact mechanism cannot be determined unequivocally the mechanism involving the removal of the proton or deuteron attached to nitrogen appears to be the rate-determining step.

5. A method of eliminating certain of the proposed mechanisms, through synthesis and measurement of the rate of decomposition of heavy nitramid in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures, has been proposed.

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AN ATTEMPT TO EXTEND THE STATISTICAL THEORY OF PERFECT SOLUTIONS.

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1. Introduction.

An attempt will be made in this note to extend the statistical theory of perfect solutions¹ to liquid mixtures in which the molecules are distinctly unequal in size. This requires us to study the combinatory factor in the partition function for a liquid mixture of such unequal molecules, which can scarcely be achieved by direct attack. The approximation used here for studying the combinatory factor is to reduce the liquid arrangements to those of a simple regular lattice and to represent a change of size by taking one molecule twice the other and allowing, or rather requiring, it to occupy two adjacent lattice points.

¹ Guggenheim, *Proc. Roy. Soc., A*, 1932, **135**, 181; 1935, **148**, 304, esp. pp. 304-308.

The calculations thus apply strictly (so far as they go) to a crystalline solid, and only by inference to a liquid mixture, in so far as its configurations can be represented by the crystalline approximation. The error in this approximation is unfortunately unknown.

The partial vapour density curves for an ordinary perfect solution of molecules of equal sizes are straight lines, the vapour densities being linear functions of the fractional concentration. The result of the extended discussion here undertaken is to show that mere change of size is sufficient to cause deviations from linearity, of the general type

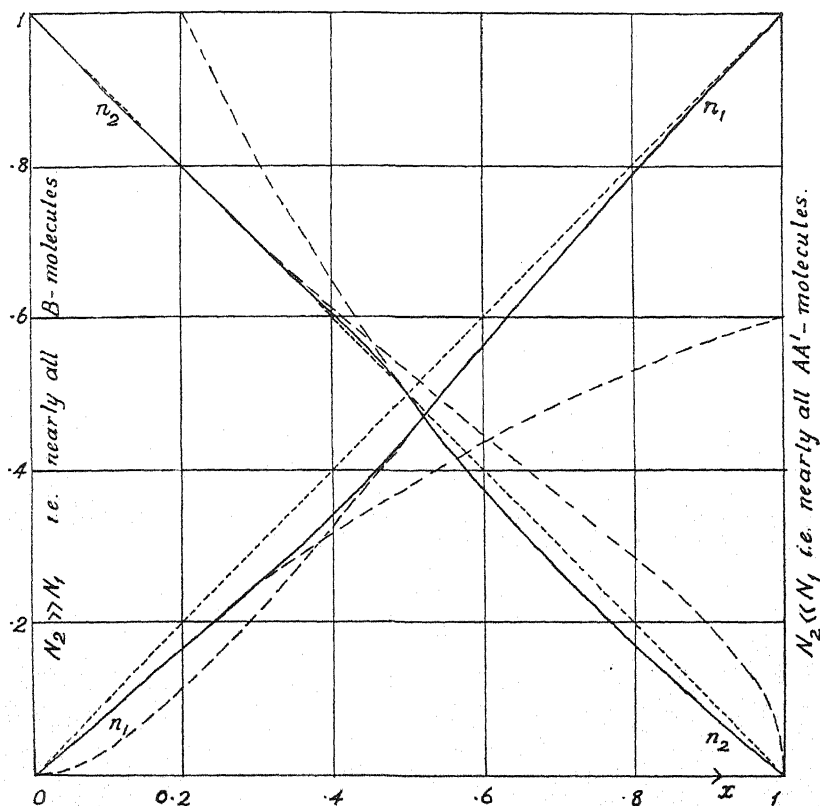


FIG. 1.—Partial vapour density curves for a mixture of N_1 double molecules (AA') and N_2 single molecules (B), as functions of the fractional concentration x . The broken curves are approximations valid for $x \ll 1$ and $1 - x \ll 1$ respectively. The continuous curves represent the best results of this investigation. The data for which they are drawn are explained in § A 10.

shown in Fig. 1; though definite, the deviation is unexpectedly small for so large a change of size. The methods used to estimate certain numerical factors are described in the appendix at the end of this note. It will be seen that these factors have not yet been estimated with any great precision, but the accuracy attained probably suffices to establish the deviations from linearity in the vapour density curves.

We summarise the well-known results for molecules of equal size for ease of reference.¹ The number of distinguishable configurations of two sets of N_1 and N_2 molecules on $N_1 + N_2$ lattice points is

$(N_1 + N_2)/(N_1! N_2!)$. Each molecule possesses a partition function, v_1 or v_2 , for its excursions about a given lattice point. In its standard state in any configuration the energy of the liquid is built up of interaction energies ϵ_{aa} , ϵ_{bb} and ϵ_{ab} between the various types of pairs of nearest neighbours. For perfect solutions

$$\epsilon_{ab} = \frac{1}{2}\epsilon_{aa} + \frac{1}{2}\epsilon_{bb}, \quad \dots \quad (1)$$

and the standard energy of all configurations is the same. The complete partition function for the solution² has the form

$$\frac{(N_1 + N_2)!}{N_1! N_2!} e^{-(N_1\epsilon_1 + N_2\epsilon_2)/kT} v_1^{N_1} v_2^{N_2} \quad \dots \quad (2)$$

[We have written ϵ_1 , ϵ_2 for $\frac{1}{2}z\epsilon_{aa}$ and $\frac{1}{2}z\epsilon_{bb}$, z being the number of nearest neighbours of each molecule in the liquid.]

The free energy of Helmholtz for the liquid and vapour phases is

$$F_l = -kT \left[(N_1 + N_2) \log (N_1 + N_2) - N_1 \log N_1 - N_2 \log N_2 - \frac{\epsilon_1 N_1 + \epsilon_2 N_2}{kT} + N_1 \log v_1 + N_2 \log v_2 \right] \quad (3)$$

$$F_v = kT \left[N_1' \log \frac{V' f_1'(T)}{N_1'} + N_1' + N_2' \log \frac{V' f_2'(T)}{N_2'} + N_2' \right] \quad (4)$$

These equations lead at once to the linear forms

$$n_1' = (n_1')_0 \frac{N_1}{N_1 + N_2}, \quad n_2' = (n_2')_0 \frac{N_2}{N_1 + N_2} \quad \dots \quad (5)$$

characteristic of perfect solutions, where n_1' , n_2' are the partial densities in the vapour phase and the suffix₀ refers to the vapour density of the pure liquids.

2. Recapitulation of the above Assumptions.

The standard equations (5), for perfect solutions, have been derived on the following assumptions:—

(i) The possible standard configurations of the liquid mixture can all be derived from any one possible configuration by simple permutations of the molecules. On these standard configurations the vibrations, etc., of the individual molecules are superposed. [This is the precise form of the usual assumption that the two sorts of molecule are the same size and have the same average number of nearest neighbours.]

(ii) The energy of the mixture in some standard state of motion, for example, when all the molecules are as nearly as possible at rest in positions of minimum potential energy, is the same for all configurations. [If the energy can be expressed as a sum of interaction energies contributed by pairs of nearest neighbours this is equivalent to the condition $\epsilon_{ab} = \frac{1}{2}\epsilon_{aa} + \frac{1}{2}\epsilon_{bb}$. The assumption also implies a zero heat of mixing at zero temperatures.]

(iii) The liquid state partition functions, v_1 and v_2 , for vibrations, etc., of the liquid molecules, including their quasi-volume factors, are the same for all configurations. [This assumption implies a zero volume change on mixing and extends the implication of zero heat of mixing to all temperatures.]

² Fowler, *Statistical Mechanics*, 1936, 2nd ed., 534.

3. Extension to a more General Model.

It is now of some interest to see whether any vapour density equations so simple as (5) can be derived when assumptions (i), (ii) and (iii) are in any way relaxed. It is difficult to see how to relax them satisfactorily by any continuous process, but we shall instead examine as best we can the effect of the abrupt change to a solution in which the molecules of one set are of dumbbell shape and occupy twice the volume of the other—more exactly are of a shape equivalent to two of the other set in their normal closest contact.

To make the problem tractable we must assume that we may enumerate the liquid configurations as if they were configurations of a crystal in which every molecule occupies a definite lattice point or lattice points. This makes no difference to the enumeration of configurations in the easier case of equal molecules, and it seems unlikely to make any serious difference even here. The absence of regularity at long ranges in the liquid as compared with the solid should not affect the total number of possible configurations as a function of N_1 and N_2 , which is all we are concerned with here.

We start by enquiring what conditions are to be satisfied here in place of (ii) in order that, speaking roughly, the liquids may mix without heat evolution or absorption. If we denote the double molecules by AA' and the others by B , and assume as usual that the energy of any standard configuration may be expressed as the sum of contributions by each pair of nearest neighbours excluding the N_1 pairs contributed by the bonds internal to the AA' molecules themselves, there are now six pairs of neighbours to consider, AA , $A'A'$, BB , AA' , $A'B$ and BA ; let x_{aa} , $x_{a'a'}$, x_{bb} , $x_{aa'}$, $x_{a'b}$, and x_{ba} be the numbers of such pairs in any configuration in a mixture of N_1 AA' 's and N_2 B 's, and let ϵ_{aa} , $\epsilon_{a'a'}$, ϵ_{bb} , $\epsilon_{aa'}$, $\epsilon_{a'b}$, and ϵ_{ba} be the energy contributions of each type of pair respectively. Then the standard energy of the configuration is

$$x_{aa}\epsilon_{aa} + x_{a'a'}\epsilon_{a'a'} + x_{bb}\epsilon_{bb} + x_{aa'}\epsilon_{aa'} + x_{a'b}\epsilon_{a'b} + x_{ba}\epsilon_{ba}.$$

We shall now suppose that each A , A' or B has on the average z nearest neighbours, of which for the A end of an AA' -molecule one neighbour is its own combined A' . There are therefore for each A $z-1$ free neighbours, for each A' , $z-1$, and for each B , z . The total number of pairs of free neighbours is $\frac{1}{2}z(2N_1 + N_2) - N_1$ or $(z-1)N_1 + \frac{1}{2}zN_2$. We have also the relations

$$\left. \begin{aligned} (z-1)N_1 &= 2x_{aa} + x_{ba} + x_{aa'} \\ (z-1)N_1 &= 2x_{a'a'} + x_{a'b} + x_{aa'} \\ zN_2 &= 2x_{bb} + x_{a'b} + x_{ba} \end{aligned} \right\} \quad . \quad . \quad . \quad (6)$$

obtained by counting up in two ways the number of free neighbours of all A 's, all A' 's and all B 's respectively. Using these relations to eliminate x_{aa} , $x_{a'a'}$ and x_{bb} from the configurational energy above, we obtain the expression

$$\begin{aligned} \frac{1}{2}(z-1)N_1(\epsilon_{aa} + \epsilon_{a'a'}) + \frac{1}{2}zN_2\epsilon_{bb} + x_{aa'}(\epsilon_{aa'} - \frac{1}{2}\epsilon_{aa} - \frac{1}{2}\epsilon_{a'a'}) \\ + x_{a'b}(\epsilon_{a'b} - \frac{1}{2}\epsilon_{a'a'} - \frac{1}{2}\epsilon_{bb}) + x_{ba}(\epsilon_{ba} - \frac{1}{2}\epsilon_{bb} - \frac{1}{2}\epsilon_{aa}) \quad . \quad (7) \end{aligned}$$

It seems likely that in such a mixture $x_{aa'}$, $x_{a'b}$ and x_{ba} are independently variable among the different configurations. If therefore all configurations are to have the same energy it is necessary and sufficient that

$$\epsilon_{aa'} = \frac{1}{2}\epsilon_{aa} + \frac{1}{2}\epsilon_{a'a'}, \quad \epsilon_{a'b} = \frac{1}{2}\epsilon_{a'a'} + \frac{1}{2}\epsilon_{bb}, \quad \epsilon_{ba} = \frac{1}{2}\epsilon_{bb} + \frac{1}{2}\epsilon_{aa} \quad (8)$$

Equations (8) are the required generalisation of (1), a result which is physically almost obvious without calculation.

We shall next consider the necessary generalisation of (iii). This retains its old form. We assume that there are liquid partition functions v_1 and v_2 for each molecule which are the same for all configurations. We have, however, now to specify carefully what are distinct configurations. This is partly a matter of convenience. We shall find it convenient to count as distinct configurations configurations in which the A-end for example, of an AA'-molecule is assigned to one lattice point while the end A' occupies two different points among the z neighbours of the points occupied by the A-end. The liquid partition function v_1 is defined to conform to this convention so that it takes care only of the vibrations about a configuration in which both ends of the AA'-molecule remain assigned to two given lattice points. Applying this rule systematically we shall count as distinct configurations configurations in which any AA' molecule is turned end for end. If the molecule AA' is symmetrical these configurations are not distinct and the double counting so arising is eliminated when necessary by the use of a symmetry number σ . A configuration is then an arrangement in which each molecule AA' is assigned to a pair of neighbouring lattice points and the B's to the remainder. A configuration may be specified by assigning the AA'-bonds to points half-way between two lattice points in such a way that no lattice point has more than one neighbouring bond point occupied, and filling up the remaining lattice points, which have no neighbouring bond point occupied, with B's. Any exchange of an A and an A', an A' and a B, or an A and a B, or any shift of an occupied bond point means a new distinct configuration. Relative to each such distinct configuration there are assumed to be liquid partition functions v_1 and v_2 independent of the configuration.

4. The Number of AA' and B Configurations.

We now come to what is of course the crux of the whole problem—the enumeration of the number of distinct configurations in which N_1 AA's and N_2 B's occupy $2N_1 + N_2$ lattice points in any sort of regular array in which each lattice point has z nearest neighbours, each AA' occupies two neighbouring lattice points and each B one only. Clearly this number is a function of N_1 , N_2 , and the geometry of the lattice. We have not been able to evaluate it completely except when $N_1 \ll N_2$, that is for a dilute solution of AA's in B's. But its form for $N_2 \ll N_1$ has, we think, probably been correctly guessed with only a small uncertainty in a numerical factor. Knowing the two extreme forms one can estimate the nature of its variation for all values of N_1/N_2 with reasonable confidence.

5. The Number of Configurations when $N_1 \ll N_2$.

We shall now examine the case $N_1 \ll N_2$, proceeding by first distributing the N_1 AA'-molecules on the lattice points and filling up with the B's. For the first molecule the A-end, say, can be placed in $2N_1 + N_2$ ways and then the A'-end in z ways in general. We can ignore the reduction in z for those comparatively few occasions when A is placed on a boundary lattice point. To a first approximation the A-end of the second AA'-molecule can then be placed in $2N_1 + N_2 - 2$ ways,

and the A'-end again in z ways. To this approximation therefore the N_1 AA'-molecule can be arranged on the lattice points in

$$(N_2 + 2N_1)(N_2 + 2N_1 - 2) \dots (N_2 + 2)z^{N_1}$$

ways, which are, of course not all distinct configurations. We must remove permutations of the N_1 AA'-molecules among themselves by dividing by $N_1!$ and redundant orientations of each molecule (if any) by dividing by σ^{N_1} . The total number ϕ of distinct configurations to this approximation is therefore given by

$$\phi = \left(\frac{2z}{\sigma}\right)^{N_1} \frac{(\frac{1}{2}N_2 + N_1)!}{(\frac{1}{2}N_2)! N_1!} \quad (9)$$

This estimate of ϕ is too large for the following reasons. When one AA' has been placed in position it has z' nearest neighbours among the lattice points and for each of these lattice points there are only z'' free nearest neighbours. For a simple square or cubic lattice or for a body-centred cubic lattice $z' = 2(z - 1)$; for other lattices it may be less; for the named lattices $z'' = z - 1$; for other arrays z'' may have more than one value for different types of neighbour, but its average value is all we require and that is definite. For a plane triangular array, for example, $z = 6$, $z' = 8$, $z'' = 4.75$, for cubic close packing $z = 12$, $z' = 18$, $z'' = 10\frac{2}{3}$. Thus, when there have been X AA'-molecules inserted we have free, to the next approximation, $2N_1 + N_2 - (z' + 2)X$ lattice points with the full quota z of free neighbours, and $z'X$ lattice points with only z'' neighbours. Thus the next AA'-molecule can be inserted, not in $z(2N_1 + N_2 - 2X)$ ways, but more nearly in

$$\begin{aligned} & \{2N_1 + N_2 - (z' + 2)X\}z + z'Xz'', \\ \text{or} \quad & z(2N_1 + N_2 - 2X) - z'(z - z'')X \end{aligned} \quad (10)$$

ways. There is therefore in ϕ an extra factor

$$1 - \frac{z'(z - z'')X}{z(2N_1 + N_2 - 2X)}$$

for this stage, and a complete extra factor

$$\prod_{x=0}^{N_1-1} \left\{ 1 - \frac{z'(z - z'')X}{z(2N_1 + N_2 - 2X)} \right\} \quad (11)$$

We have neglected triple and higher order interferences, so that these factors are only correct to the first order in X . They are therefore equivalent to

$$\begin{aligned} & 1 - \frac{z'(z - z'')}{z} \sum_{x=0}^{N_1-1} \frac{X}{2N_1 + N_2}, \\ \text{or} \quad & 1 - \frac{z'(z - z'')}{z} \frac{\frac{1}{2}N_1(N_1 - 1)}{2N_1 + N_2}. \end{aligned} \quad (12)$$

The function of interest is $\log \phi$. By (9) we have

$$\begin{aligned} \log \phi = & (\tfrac{1}{2}N_2 + N_1) \log (\tfrac{1}{2}N_2 + N_1) \\ & - \tfrac{1}{2}N_2 \log \tfrac{1}{2}N_2 - N_1 \log N_1 + N_1 \log 2z/\sigma \end{aligned} \quad (13)$$

By (12) this must be corrected by the addition of the extra term

$$- \frac{z'(z - z'')}{2z} \frac{N_1^2}{2N_1 + N_2} \quad (14)$$

6. The Number of Configurations when $N_2 \ll N_1$, in particular when $N_2 = 0$.

Let us start with $N_2 = 0$ and try to estimate in how many distinguishable ways N_1 AA'-molecules can be placed on $2N_1$ lattice points. Formula (9) makes it clear at once that an upper bound to the number, obtained by putting $N_2 = 0$ there, is $(2z/\sigma)^{N_1}$. It is, however, also clear that this bound is likely to be so widely in excess as not to be of much value. The factor σ^{-N_1} needs no comment, and we may clearly expect that the required number will be of the form $(z'''/\sigma)^{N_1}$ where z''' is some definite function of the lattice type. The attempt to get a closer estimate of z''' leads us rather far afield and is described in the appendix. It there appears that it is probable that $z''' < z$ but that z is not greatly in excess. We shall continue the general discussion of the problem on this basis, namely that

$$\log \phi = N_1 \log z'''/\sigma \quad (z''' < z). \quad (15)$$

We can now write down a first approximation to the number of distinct configurations when $N_2 \neq 0$, but $N_2 \ll N_1$. We can arrange the B-molecules first in

$$\frac{(2N_1 + N_2)!}{N_2! (2N_1)!}$$

ways on the lattice points. To this approximation we may suppose that the few occupied points make no difference to the number of ways of arranging the AA'-molecules, which can therefore be arranged in $(z'''/\sigma)^{N_1}$ ways. We thus find that

$$\log \phi = (2N_1 + N_2) \log (2N_1 + N_2) - N_2 \log N_2 - 2N_1 \log 2N_1 + N_1 \log z'''/\sigma. \quad (16)$$

Formula (16) for $\log \phi$ will, of course, overestimate ϕ when N_2 increases. The studies in the appendix suggest that a better approximation will be obtained by introducing, in ϕ , a reduction factor $1/\alpha(z)$ for each B-molecule in position, *i.e.*, by adding an extra term

$$- N_2 \log \alpha(z) \quad (17)$$

to the right-hand side of equation (16). It is suggested that a rough estimate of this effect may be obtained as follows. Each occupied point has z neighbours which are to some degree like surface lattice points in that they have only $(z - 1)$ neighbours free instead of z . A surface lattice point provides an extra factor $l(z)$ in ϕ besides its normal contribution, where $l(z) < 1$. The value of $l(z)$ differs from unity by a moderate factor which is estimated in the appendix. We may thus expect an extra factor $\{l(z)\}^z$ in ϕ for each B-molecule in position, *i.e.*, an extra term in $\log \phi$ of the form (17) with $\alpha(z) = \{l(z)\}^{-z}$.

7. The Vapour Density Equations.

We can now write down the free energy of Helmholtz for the liquid in the form

$$F_l = -kT \left[\log \phi - \frac{\epsilon_1 N_1 + \epsilon_2 N_2}{kT} + N_1 \log v_1 + N_2 \log v_2 \right], \quad (18)$$

from which we can at once deduce the vapour density equations, using (4) for F_v . We find that

$$\left. \begin{aligned} n_1' &= \frac{f_1'}{v_1} e^{\epsilon_1/kT} \exp \left(-\frac{\partial \log \phi}{\partial N_1} \right) \\ n_2' &= \frac{f_2'}{v_2} e^{\epsilon_2/kT} \exp \left(-\frac{\partial \log \phi}{\partial N_2} \right) \end{aligned} \right\} \quad (19)$$

To these we may add the formulæ for the pure liquids, namely,

$$(n_1')_0 = \frac{\sigma f_1'}{z''' v_1} e^{\epsilon_1/kT}, \quad (n_2')_0 = \frac{f_2'}{v_2} e^{\epsilon_2/kT}. \quad (20)$$

These equations follow at once from (19) using the limiting values of $\log \phi$, $N_1 \log z'''/\sigma$ and 0 respectively. On combining (19) and (20) we find

$$n_1' = \frac{z'''}{\sigma} (n_1')_0 \exp \left(-\frac{\partial \log \phi}{\partial N_1} \right), \quad (21)$$

$$n_2' = (n_2')_0 \exp \left(-\frac{\partial \log \phi}{\partial N_2} \right). \quad (22)$$

There are now two cases to consider.

Case (i).— $N_1 \ll N_2$; $\log \phi$ given by (13) and (14). We have

$$\frac{\partial \log \phi}{\partial N_1} = \log \left(\frac{1}{2} N_2 + N_1 \right) - \log N_1 + \log \frac{2z}{\sigma} - \frac{z'(z-z'')}{z} \frac{N_1(N_1+N_2)}{(2N_1+N_2)^2},$$

so that

$$n_1' = (n_1')_0 \frac{z'''}{z} \frac{N_1}{N_2 + 2N_1} \exp \left\{ \frac{z'(z-z'')}{z} \frac{N_1(N_1+N_2)}{(2N_1+N_2)^2} \right\}. \quad (23)$$

We have also

$$\frac{\partial \log \phi}{\partial N_2} = \frac{1}{2} \log \left(\frac{1}{2} N_2 + N_1 \right) - \frac{1}{2} \log \frac{1}{2} N_2 + \frac{z'(z-z'')}{2z} \frac{N_1^2}{(2N_1+N_2)^2},$$

so that

$$n_2' = (n_2')_0 \left(\frac{N_2}{N_2 + 2N_1} \right)^{\frac{1}{2}} \exp \left\{ -\frac{z'(z-z'')}{2z} \frac{N_1^2}{(2N_1+N_2)^2} \right\}. \quad (24)$$

To reduce these to standard forms we put

$$\frac{N_1}{N_1 + N_2} = x, \quad \frac{N_2}{N_1 + N_2} = 1 - x.$$

Then

$$\left. \begin{aligned} n_1' &= (n_1')_0 \frac{z'''}{z} \frac{x}{1+x} \exp \left\{ \frac{z'(z-z'')}{z} \frac{x}{(1+x)^2} \right\} \\ n_2' &= (n_2')_0 \left(\frac{1-x}{1+x} \right)^{\frac{1}{2}} \exp \left\{ -\frac{z'(z-z'')}{2z} \frac{x^2}{(1+x)^2} \right\} \end{aligned} \right\} (x \ll 1) \quad (25)$$

Case (ii).— $N_2 \ll N_1$; $\log \phi$ given by (16) and (17). We have

$$\frac{\partial \log \phi}{\partial N_1} = 2 \log (2N_1 + N_2) - 2 \log 2N_1 + \log z'''/\sigma,$$

so that

$$n_1' = (n_1')_0 \left(\frac{2N_1}{N_2 + 2N_1} \right)^2. \quad (26)$$

We have also

$$\frac{\partial \log \phi}{\partial N_2} = \log (2N_1 + N_2) - \log N_2 - \log \alpha(z),$$

so that

$$n_2' = (n_2')_0 \frac{N_2}{2N_1 + N_2} \alpha(z); \quad (27)$$

therefore we have

$$\left. \begin{aligned} n_1' &= (n_1')_0 \left(\frac{2x}{1+x} \right)^2 \\ n_2' &= (n_2')_0 \left(\frac{1-x}{1+x} \right) \cdot \alpha(z) \end{aligned} \right\} \quad (1-x \ll 1). \quad (28)$$

Fig. 1 shows these curves as broken lines for values of the constants z''' and $\alpha(z)$ as estimated in the appendix. The continuous curves in Fig. 1 are suggested as the (roughly) correct vapour density curves for all values of x .

8. Discussion of the Curves and Conclusion.

The well-known equation connecting these curves

$$\frac{\partial n_1'}{\partial x} \bigg/ \frac{\partial n_2'}{\partial (1-x)} = \frac{n_1'/x}{n_2'/(1-x)} \quad (29)$$

is automatically satisfied by the partial vapour densities of equations (25) and (28), whatever the values of z''' , $\alpha(z)$, etc. This is because the equation (29) is simply a mathematical consequence of assuming that the free energy F (which we have used in accordance with thermodynamical principles) is an extensive property of the liquid phase: and the expression (18) may be put in the form

$$F_i = -kT \left\{ -\frac{\epsilon_1 x + \epsilon_2 (1-x)}{kT} + x \log v_1 + (1-x) \log v_2 + \frac{1}{2}(1+x) \log \frac{1}{2}(1+x) - \frac{1}{2}(1-x) \log \frac{1}{2}(1-x) - x \log x + x \log 2z/\sigma - \frac{z'(z-z''')}{z} \frac{x^2}{1+x} \right\} (N_1 + N_2), \quad (x \ll 1),$$

and

$$F_i = -kT \left\{ -\frac{\epsilon_1 x + \epsilon_2 (1-x)}{kT} + x \log v_1 + (1-x) \log v_2 + (1+x) \log (1+x) - (1-x) \log (1-x) - 2x \log 2x + x \log z'''/\sigma - (1-x) \log \alpha(z) \right\} (N_1 + N_2), \quad (1-x \ll 1),$$

when this characteristic is clearly shown. (The property was implied in our assumptions concerning the form of ϕ , e.g., that the influence of the B-molecules when $N_1 \gg N_2$ is $[1/\alpha(z)]^{N_2}$ and not, say, $[1/\alpha(z)]^{N_2^2}$). $\partial F_i/\partial N_1$ and $\partial F_i/\partial N_2$ are then intensive expressions depending only on the relative concentration x and not on the extent of the liquid phase.

The passage from the curves given by equations (25) to those of equations (28) must be in accord with (29). In particular, this means that the deviations from the curves (25) must occur for both n_1' and n_2' at the same relative concentration x ; and the equations (28) for n_1' and n_2' when $1-x \ll 1$ must become valid together. This affords considerable guidance for sketching the vapour density curves for all values of x .

The particular nature of the model we have assumed for the liquid mixture is clearly shown in the resulting partial vapour density equations and curves.

Consider, for example, the partial vapour density of the AA'-molecules, n_1' ; this depends on z when $x \ll 1$, *i.e.*, when there are few AA'-molecules in the mixture and they are free to turn without impeding each other, and on z''' when $1 - x \ll 1$, *i.e.*, when the mixture consists mainly of AA' molecules and, on our lattice hypothesis, these cramp each other's freedom.

The partial vapour density n_2' also behaves appropriately. In particular we notice that the curves approximate very closely to straight lines when $x \ll 1$ and the difference in size of the molecules is relatively unimportant; n_2' is then independent of the lattice frame while $\partial n_1' / \partial x$ differs from the value $(n_1')_0$ —which it would have were the molecules of equal size—only by the factor z'''/z due to $(n_1')_0$ being the vapour density of a pure liquid of AA'-molecules.

The above investigations show that non-linear partial vapour density curves of a binary liquid mixture may be due to the components of the mixture differing widely in molecular size and are not necessarily due to intermolecular forces except in so far as these forces determine the structure of the whole liquid.

APPENDIX.

A1. Estimates of z''' : Nature of the Problem.

The only means apparently available of obtaining information about the number of distinguishable arrangements of N_1 AA'-molecules on $2N_1$ lattice points is to study numerically certain simple arrays in a plane for which z''' can actually be determined.

Throughout the appendix we assume that the molecules are symmetrical, so that turning any of them end for end does not produce a new configuration. This is equivalent to putting $\sigma = 2$. If in such circumstances we can express the number of distinct configurations in the form λ^{N_1} , N_1 being supposed large, then in the general case we have only to replace λ by $2\lambda/\sigma$, and $z''' = 2\lambda$.

It will be convenient to call λ the molecular freedom.

We shall find that it is possible, without undue labour, to determine λ for long plane strips of lattice points in square array ($z = 4$) and of width any number of points up to 6, and also for long plane strips of lattice points in triangular array ($z = 6$) and of width any number of points up to 4. These strips are too narrow for their molecular freedoms very nearly to equal those for the corresponding regular arrays covering the whole plane. But we can estimate the undue restriction of the boundaries by considering also similar arrays on a circular cylinder, when the long boundaries are eliminated.

It seems possible in this way to make quite reliable estimates of z''' for two dimensional arrays. No similar direct estimates can be made for three dimensional arrays, but for some of these the molecular freedoms can probably be estimated, sufficiently accurately, by indirect methods (§§ A6, A7).

The determination of λ for a strip of given width requires, as we shall show in § A2, the solution of a set of simultaneous linear difference equations. These rapidly become of very high order as the width of the strip increases, and such reliable progress as we have been able to make is largely due to the use [$z = 4$, plane strip of width 6] of Mallock's equation solving machine. This machine is perfectly adapted for the problem, as we only require to determine the largest root of an equation in determinantal form, the terms of the determinant being simple polynomials in the unknown whose value is required. We have to thank Mr. Mallock most

heartily for leave to work on the machine, and for his kindness in instructing one of us in its use.

A2. Long Flat Strips of Lattice Points in Square Array.

The width of the strip is denoted by s .

The nature of the difference equations will be sufficiently illustrated by considering in detail the cases $s = 2, 4$.

Example (i). $s = 2$.

Let V_n be the number of distinct arrangements of n symmetrical molecules of type AA on the $2n$ points of a $2 \times n$ strip.

We obtain a difference equation for V_n by considering the possible ways of inserting the last molecules (at one end of the strip).

The strip of length $n + 1$ can end only in the ways shown.

$$\begin{array}{ccc}
 & \times & \times & & \times & \times & (n-1) \\
 & & & & & & \\
 (n) & \times & \times & & \times & \times & (n) \\
 & & & & | & | & \\
 (n+1) & \times & -\times & & \times & \times & (n+1).
 \end{array}$$

A cross specifies a lattice point and a connecting line specifies a molecule in position. The left-hand configuration can be realised in V_n ways and the right-hand one in V_{n-1} ways. Therefore

$$V_{n+1} = V_n + V_{n-1}.$$

This difference equation is solved by

$$V_n = v_1 \mu_1^n + v_2 \mu_2^n,$$

where μ_1 and μ_2 are the roots of the equation

$$\mu^2 - \mu - 1 = 0,$$

and v_1 and v_2 are determined to fit the initial conditions

$$V_1 = 1, V_2 = 2.$$

The roots are

$$\frac{1}{2}(1 \pm \sqrt{5}).$$

For our strip, however, n is assumed to be very large, and so if μ is the greater of μ_1 and μ_2 we shall have, with negligible error,

$$V_n = v\mu^n$$

and since, for this strip, the number of AA molecules $N_1 = n$, the molecular freedom is given by (n being large)

$$\lambda_s \simeq (v\mu^n)^{1/n} \simeq \mu = \frac{1}{2}(1 + \sqrt{5}) = 1.618.$$

The suffix to λ denotes the width of the strip.

Example (ii). $s = 4$.

This case is slightly more complicated and leads to a set of three simultaneous difference equations.

Let V_n , A_n and B_n be the numbers of distinct arrangements for the arrays

$$\begin{array}{ccc}
 \dots\dots\dots & \dots\dots\dots & \dots\dots\dots \\
 \times \times \times \times & \times \times \times \times & \times \times \times \times \\
 \times \times \times \times (n-1) & \times \times \times \times (n-1) & \times \times \times \times (n-1) \\
 \times \times \times \times (n) & \times \times (n) & \times \times (n)
 \end{array}$$

respectively. They also serve to identify the arrays.

Then all the possible distinct endings for V_{n+1} are

$$\begin{array}{ccccc}
 \cdot & \cdot & \cdot & \cdot & \cdot \\
 \times \times \times \times & \times \times \times \times & \times \times \times \times & & \\
 \times \times \times \times (n) & \times \times \times \times (n) & \times \times \times \times (n) & & \\
 \times - \times \times - \times (n+1) & \times - \times \times \times (n+1) & \times \times - \times \times (n+1) & & \\
 & \cdot & \cdot & \cdot & \cdot \\
 & \times \times \times \times & \times \times \times \times & & \\
 & \times \times \times \times (n) & \times \times \times \times (n) & & \\
 & \times \times \times - \times (n+1) & \times \times \times \times (n+1) & &
 \end{array}$$

so that

$$V_{n+1} = V_n + 2A_n + B_n + V_{n-1} \quad \text{A. (1)}$$

The possible endings for A_{n+1} are

$$\begin{array}{ccccc}
 \cdot & \cdot & \cdot & \cdot & \cdot \\
 \times \times \times \times & \times \times \times \times & & & \\
 \times \times \times \times (n) & \times \times \times \times (n) & & & \\
 \times - \times (n+1) & \times \times (n+1) & & &
 \end{array}$$

so that

$$A_{n+1} = V_n + A_n \quad \text{A. (2)}$$

And finally, the possible endings for B_{n+1} are

$$\begin{array}{ccccc}
 \cdot & \cdot & \cdot & \cdot & \cdot \\
 \times \times \times \times & \times \times \times \times & & & \\
 \times \times \times \times (n) & \times \times \times \times (n) & & & \\
 \times - \times (n+1) & \times \times (n+1) & & &
 \end{array}$$

so that

$$B_{n+1} = V_n + B_{n-1} \quad \text{A. (3)}$$

The simultaneous equations (A, 1, 2, 3) can be solved in the usual way by the substitution

$$V_n = v\mu^n, A_n = a\mu^n, B_n = b\mu^n$$

(or sums of such terms), which leads to the determinantal equation for μ

$$\begin{vmatrix}
 -\mu^2 + \mu + 1 & 2\mu & \mu \\
 1 & -\mu + 1 & 0 \\
 \mu & 0 & -\mu^2 + 1
 \end{vmatrix} = 0.$$

The determinant reduces to

$$(\mu - 1)(\mu^4 - \mu^3 - 5\mu^2 - \mu + 1) = 0,$$

of which the largest root is $\mu = 2.84$.

Since in this case the number of AA molecules $N_1 = 2n$, the molecular freedom is given by

$$\lambda_1 \cong (v\mu^n)^{1/2n} \cong \sqrt{2.84} = 1.685.$$

The method of dealing with such strips should now be apparent.

The flat strip of lattice points in square array $n \times 6$ leads to a set of 9 difference equations, and so to a 9-row determinant. The greatest

root of this has been determined by Mallock's equation solver to be $\mu = 5.057$. Since for this array $N_1 = 3n$ the molecular freedom is given by

$$\lambda_6 = \sqrt[3]{5.057} = 1.716.$$

The strip $n \times 8$ leads to a set of equations which can fairly easily be reduced in number to eighteen, but no attempt has yet been made to solve these. Strips $n \times 3$, and $n \times 5$, have also been considered. In such cases, when n is odd there is an odd number of lattice points and only $\frac{1}{2}(3n-1)$, or $\frac{1}{2}(5n-1)$, molecules can be accommodated. We form difference equations just as for even widths, always completing the working end, which implies that the free lattice point is pushed back to the beginning. This vacancy, however, will not disturb the molecular freedom for long strips, and the λ 's which we calculate will be strictly comparable with those for even widths.

All these results are given in Table I.

A3. Long Strips of Lattice Points in Square Array Round a Cylinder.

Square arrays on a cylinder are simpler than those on a plane, since the cyclic nature of the array eliminates differences between endings such as A_n and B_n of example (ii). We can best illustrate this by working through the case $s = 4$ again in detail.

Let V_n and A_n be the numbers of distinct arrangements for the arrays

$$\begin{array}{cc} \cdot & \cdot \\ \times \times \times \times & \times \times \times \times \\ \times \times \times \times (n-1) & \times \times \times \times (n-1) \\ \times \times \times \times (n) & \times \times (n) \end{array}$$

respectively. Then all the possible distinct endings for V_{n+1} are

$$\begin{array}{cccc} \cdot & \cdot & \cdot & \cdot \\ \times \times \times \times & \times \times \times \times & \times \times \times \times & \times \times \times \times \\ \times \times \times \times (n) & \times \times \times \times (n) & \times \times \times \times (n) & \times \times \times \times (n) \\ \times - \times \times - \times (n+1) & \times - \times \times \times (n+1) & \times \times - \times \times (n+1) & \times \times \times - \times (n+1) \\ \cdot & \cdot & \cdot & \cdot \\ \times \times \times \times & \times \times \times \times & \times \times \times \times & \\ \times \times \times \times (n) & \times \times \times \times (n) & \times \times \times \times (n) & \\ \begin{array}{|c|c|c|c|} \hline \times & \times & \times & \times \\ \hline \end{array} (n+1) & \begin{array}{|c|c|c|c|} \hline \times & \times & \times & \times \\ \hline \end{array} (n+1) & \begin{array}{|c|c|c|c|} \hline \times & \times & \times & \times \\ \hline \end{array} (n+1) & \end{array}$$

so that

$$V_{n+1} = 2V_n + V_{n-1} + 4A_n.$$

The possible endings for A_{n+1} are

$$\begin{array}{cc} \cdot & \cdot \\ \times \times \times \times & \times \times \times \times \\ \times \times \times \times (n) & \times \times \times \times (n) \\ \times - \times (n+1) & \times \times (n+1), \end{array}$$

so that

$$A_{n+1} = V_n + A_n.$$

These equations lead to the equation for μ (now, strictly, denoted by μ^c)

$$\mu^3 - 3\mu^2 - 3\mu + 1 = 0$$

of which the greatest root is $\mu = 3.732$,

and so the molecular freedom, denoted by λ_4^c is given by

$$\lambda_4^c = \sqrt{3.732} = 1.932.$$

Owing to this greater simplicity of the cylindrical equations all widths up to and including 8 can be solved by elementary methods, without undue labour.

All these results are given in Table I.

From a study of these values, or by plotting them on a diagram, it is fairly easy to satisfy oneself that they converge, as $s \rightarrow \infty$, to a value which must be quite near 1.8.

The values for odd and even s form separate sequences: the λ_{odd}^c sequence and both the λ_s sequences approach the limit from below, while the λ_{even}^c sequence approaches it from above.

TABLE I.—VALUES OF THE MOLECULAR FREEDOM λ FOR LONG STRIPS OF LATTICE POINTS IN SQUARE ARRAY.

Width. s .	Flat Strips.		Cylindrical Strips.	
	μ .	$\lambda_s = \mu^{2/s}$.	μ^c .	$\lambda_s^c = \mu^{2/s}$.
1	1	1	—	—
2	1.618	1.618	2.414	2.414 *
3	1.932	1.551	2.190	1.685
4	2.84	1.685	3.732	1.932
5	3.542	1.658	4.075	1.754
6	5.057	1.716	6.32	1.849
7	—	—	—	—
8	—	—	11.04	1.822

A4. Long Strips of Lattice Points in Triangular Array.

It is not necessary to give details of the calculations for these strips, except to specify that the points in a strip form a slanting array, as shown (Fig. 2). The only novelty arises from the greater variety of positions

TABLE II.—VALUES OF THE MOLECULAR FREEDOM λ FOR LONG STRIPS OF LATTICE POINTS IN TRIANGULAR ARRAY.

Width. s .	Flat Strips.		Cylindrical Strips.	
	μ .	$\lambda_s = \mu^{2/s}$.	μ^c .	$\lambda_s^c = \mu^{2/s}$.
1	1	1	—	—
2	1.618	1.618	2.732	2.732
3	2.414	1.800	3.617	2.356
4	3.717	1.928	5.65	2.377
5	—	—	8.33	2.333
6	—	—	13.1	2.357

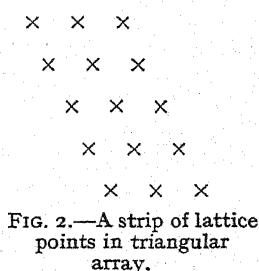
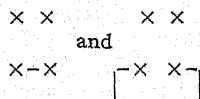


FIG. 2.—A strip of lattice points in triangular array.

* The value for λ_2^c is obtained by counting the endings and as



distinct. This is correct by analogy with the other cylindrical cases.

in which the molecules may be placed, therefore forming the greater variety of possible endings.

The results obtained are summarised in Table II.

The values probably converge, for large s , to a value close to 2.3.

A5. Raw Ends.

It is now necessary to criticise somewhat the above technique.

When considering the number of ways of arranging N_1 non-overlapping diatomic molecules on a long strip of $2N_1$ lattice points $n \times s$ we may have introduced rather rigorous end conditions. If we suppose that to cover such a strip we start somewhere near the middle and lay down molecules one by one so as to cover all the lattice points until the ends are reached, then we cannot be sure that we shall be able to use up quite all the N_1 molecules: we may be left with a few, not more than $\frac{1}{2}s$, which will not fit in. Physically this is of no importance. But in our mathematical considerations we have constrained the strip to end in rather a particular way (or ways) which may have reduced the molecular freedom. The exact nature of the trouble will be more apparent if we reconsider the strip of example (ii).

Example (ii) contd.—So far we have considered only the endings

.
x x x x	x x x x	x x x x	x x x x
x x x x	x x	x x	x x

which can be regarded as found on breaking through a fully covered strip

x x x x
. . . .
. . . .
. . . .
. . . .
x x x x

And if we consider a long strip having any of these endings (at either end) then the number of ways of completely covering it with N_1 AA-molecules is λ^{N_1} where, in this case, $\lambda = 1.685$.

But the above endings are not all the possible endings: there are also

.
x x x x (n-1)	x x x x (n-1)	x x x x (n-1)	x x x x (n-1)
x x x (n)	x x (n)	x (n)	x (n)
α_n	β_n	α_{n-1}	β_{n-1}

. . . .
and x x x x (n-1)
 x x (n)

the last of which may clearly be ignored. We have yet to consider the number of ways of just covering a long strip ending (and beginning) in any of these ways. With an obvious notation we find

$$\begin{aligned}\alpha_{n+1} &= \alpha_{n-1} + \alpha_n + \beta_n \\ \beta_{n+1} &= \alpha_n + \beta_{n-1}\end{aligned}$$

and so obtain the equation

$$\begin{vmatrix} -\mu^2 + \mu + 1 & \mu \\ \mu & -\mu^2 + 1 \end{vmatrix} = 0$$

of which the greatest root is $\mu = 2.094$. So one of these new strips can be covered by N_1 AA-molecules in $(2.094)^{\frac{1}{2}N_1} = (1.447)^{N_1}$ ways.

It is important that the molecular freedom (1.447), for this class of arrangements is less than that for the class we previously considered.

A full consideration on these lines of the molecular freedoms for the lattice arrays of §§ A2, 3, 4 leaves the results of Tables I. and II. unchanged. In every case we find that the arrangements and appropriate endings fall into distinct classes, but the class already considered, containing V_n , always corresponds to the greatest molecular freedom. More precisely, the possible endings fall into groups (ξ) , (η) , (ζ) , . . ., containing ξ , η , ζ . . . members respectively, and the number of ways of covering a long strip beginning and ending with two specified members of the same group $\leq \lambda_s^{N_1}$ where N_1 is the number of molecules used and λ_s , or λ_s^* , is the value given in Tables I. or II. If, then, we make no restriction on the endings the number of ways of covering the strip will be less than

$$\begin{aligned} (\xi^2 + \eta^2 + \zeta^2 + \dots) \lambda_s^{N_1} &\leq (\xi + \eta + \zeta + \dots)^2 \lambda_s^{N_1} \\ &= (1 + s + \binom{s}{2} + \dots)^2 \lambda_s^{N_1} \\ &= 2^{2s} \lambda_s^{N_1}. \end{aligned}$$

Now $\lim_{N_1 \rightarrow \infty} \left[2^{2s} \lambda_s^{N_1} \right]^{1/N_1} = \lambda_s$ even when s is large, since then $N_1 \sim s^2$; and

therefore the molecular freedom for the strip is correctly given by λ_s even when the ends may be raw.

A6. Extension to Three-dimensional Arrays. A Thin Slab.

We must now leave these two-dimensional arrays and try to extend the calculations to give the molecular freedoms for three-dimensional lattices.

It does not seem possible to make much progress by direct calculation, owing to the way in which the equations rapidly become unmanageable. But fortunately it has been found possible to carry through again some of the calculations of §§ A2, 3, particularly of § A3, when in each case we consider two such strips of lattice points, one above the other and the lattice distance apart. The lattice points are then in simple cubic formation.

Four cases have been solved: those corresponding to the flat strip $n \times 2$ of § A2 and the cylindrical strips $n \times 2$, $n \times 3$, $n \times 4$ of § A3.

The fact that now each strip is cut from a slab of two planes makes no essential difference to the setting up of the equations; it only makes them more complicated. The results are given in Table III. At first sight it is difficult to infer from these results the molecular freedom for the whole slab; *i.e.*, the limit of λ_s as $s \rightarrow \infty$. But a comparison of these values with the corresponding ones of Tables I. and II. suggest that the sequences they form resemble those of Table I. and tend to a limit fairly near the value 2.15.

TABLE III.—MOLECULAR FREEDOMS FOR SLABS $2 \times n \times s$.

s .	μ .	$\lambda_s = \mu^{1/s}$.
2 flat	3.732	1.932
2 cylindrical	6.855	2.62
3 „	9.355	2.107
4 „	24.4	2.222

A7. Simple Lattices with Greater Co-ordination Numbers.

It is interesting to consider the geometry of this last array. We see that it is a regular array of equivalent lattice points and none of the neighbours of any one point are neighbours of each other. For convenience we shall call this a simple lattice array. Then the slab of § A6 is a simple lattice array of co-ordination number five.

Now we have already, in Table I. and example (i) respectively, considered simple lattice arrays having co-ordination numbers 4 and 3 and found their molecular freedoms. Of course there are other simple lattices with the same co-ordination numbers: *e.g.*, for $z = 4$ there is the tetrahedral array of the diamond lattice, and we do not know that for these the freedoms will be the same.

If, however, we assume that this is so; that in fact for simple lattices the molecular freedom depends on the co-ordination number alone (and

TABLE IV.—MOLECULAR FREEDOMS FOR SIMPLE LATTICES.

Lattice.	z .	Freedom = $\lambda(z)$.
Isolated pairs of points .	1	1
A linear array . . .	2	1
Example (i) . . .	3	1.618
Square formation . . .	4	1.8
Slab of § A. 6 . . .	5	2.15

it is perhaps reasonable to suppose that a property of pairs of points will depend only on the geometry of neighbours)* then we may be able to estimate the freedom for simple cubic packing, $z = 6$, by extrapolation from the values we already know. For this purpose we draw up Table IV. In the first column we

describe the particular array from which we have calculated the corresponding molecular freedom.

We find that $\lambda(z)$ increases as z increases but the values form separate sequences according as z is odd or even. If the values are plotted on a diagram it is apparent that

$$\lambda(4) + \lambda(5) - \lambda(3) < \lambda(6) < \lambda(5) + \frac{1}{2}(\lambda(5) - \lambda(3))$$

i.e. $2.33 < \lambda(6) < 2.42$

It seems probable, in fact, that $\lambda(6)$ is about 2.38.

Naturally this is rather a rough estimate of the molecular freedom for simple cubic packing because the values we have taken for $\lambda(4)$ and $\lambda(5)$ may not be quite correct. But the results of Table II. suggest that it is not far out. In § A4 we estimated the molecular freedom for a two-dimensional array of points in triangular formation to be about 2.3. This is an array in which each point has 6 neighbours but it is not a simple array in the sense of this paragraph and we should expect the freedom to be somewhat reduced (from the $\lambda(6)$ value) on that account.

Any further extrapolation, to $z = 7, 8, \dots$, will be of doubtful value, but if we would do so, assuming that $\lambda(6) = 2.38$, we find $\lambda(7) \sim 2.65$ and $\lambda(8) \sim 2.88$. This last result is the best estimate we can make at present of the molecular freedom for body centred cubic packing. It is worth recording only because we may expect it to be comparable with, and rather greater than, the freedom for hexagonal packing with the same

* The cylindrical strips of § A3 may seem to provide an immediate exception to this hypothesis; their molecular freedoms depend on their widths s . But these lattices, by their cyclic nature, differ from those of Table IV.; they are peculiar in that after specifying the "unit cell" and directions of its repetition we have further to prescribe the length of the lattice in one such direction.

The lattices of Table IV. form the most natural sequence of lattice arrays from isolated points to a simple cubic lattice, and the extrapolated value of $\lambda(6)$ is likely to be reliable if the values listed in Table IV. are correct.

co-ordination number, Fig. 3. This array (Fig. 3) is interesting in that we may regard it as built up either of planes of points in square formation each having two neighbours in each adjacent plane or of planes of points in triangular formation each having one neighbour in each adjacent plane. If in either case, (a), (b) respectively, we consider a slab of t planes and denote the corresponding freedom by λ_t then repeated use of any formula giving λ_{2t} in terms of λ_t will lead to an estimate of the freedom for the complete three-dimensional array.

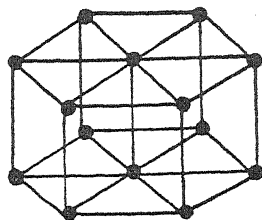


FIG. 3.

Considerations, into which we need not enter here, of the number of ways of inserting connecting molecules between two slabs, each of thickness t , suggest that a possible formula is

$$\lambda_{2t} = \lambda_t \left(1 + \frac{y}{\zeta \lambda_t} \right)^{1/t}$$

where in case (a)

$$y = 2 \text{ and } \lambda_1 = 1.8$$

and in case (b)

$$y = 1 \text{ and } \lambda_1 = 2.3.$$

ζ is a parameter which can be found from the condition that we must get the same result, $\lambda = \lim_{t \rightarrow \infty} \lambda_t$, for both (a) and (b). This gives $\zeta = 3.8$ and $\lambda = 2.81$.

Although this compares reasonably with the value for $\lambda(8)$ above, these estimates are probably too rough to have much real value.

A8. The Effect of a Few B-Molecules.

Suppose now that there are $2N_1 + N_2$ lattice points ($N_2 \ll N_1$) of which N_2 are occupied by B-molecules. We may suppose these to be so few that it makes no essential difference where they are (so that they will have the same effect in any of their $\frac{N_2!}{(2N_1 + N_2)!(2N_1)!}$ possible positions).

It will not, however, be correct to suppose that they have no effect at all on the freedom of the AA-molecules. Should we do so we should get equation (19)

$$\log \phi = (2N_1 + N_2) \log (2N_1 + N_2) - N_2 \log N_2 - 2N_1 \log 2N_1 + N_1 \log z'''/\sigma$$

but we must correct this to allow for the interference of the B-molecules with the AA-molecules.

The most obvious effect of the N_2 B-molecules is that they themselves occupy lattice points which are neighbours of zN_2 other lattice points: so that instead of an assembly of $2N_1$ lattice points of which each has z neighbours we now have an assembly of $2N_1 + N_2$ lattice points of which N_2 are occupied by B-molecules and of the remaining $2N_1$ (which are occupied by AA-molecules) zN_2 have $z - 1$ neighbours while $2N_1 - zN_2$ have z neighbours.

It is tempting then to assume that the N_1 AA-molecules can be arranged on these $2N_1$ points in

$$[\lambda(z)]^{N_1 - \frac{1}{2}zN_2} [\lambda(z-1)]^{\frac{1}{2}zN_2} \quad \dots \quad \text{A. (4)}$$

ways. But of course this is by no means justified because the two sets of lattice points (those with z and $z - 1$ neighbours respectively) do not form separate arrays, and moreover N_2 is, by hypothesis, small. If, however, we do make this assumption, we then note that A. (4) may be written as

$$[\lambda(z)]^{N_1} \left[\frac{\lambda(z-1)}{\lambda(z)} \right]^{\frac{1}{2}zN_2},$$

Of course this is a rather arbitrary way of measuring the effect of a border lattice point (as distinct from one with fully z neighbours) and our assumption that a B-molecule will behave like z border lattice points is very hypothetical. If, however, we proceed in this way we have to add to $\log \phi$ (as given in equation (19)) the term

$$-N_2 \log \alpha(z)$$

where $\alpha(z) = [l(z)]^{-z}$.

To find $l(4)$ from the data of Table I. we draw up Table VI. These values suggest that

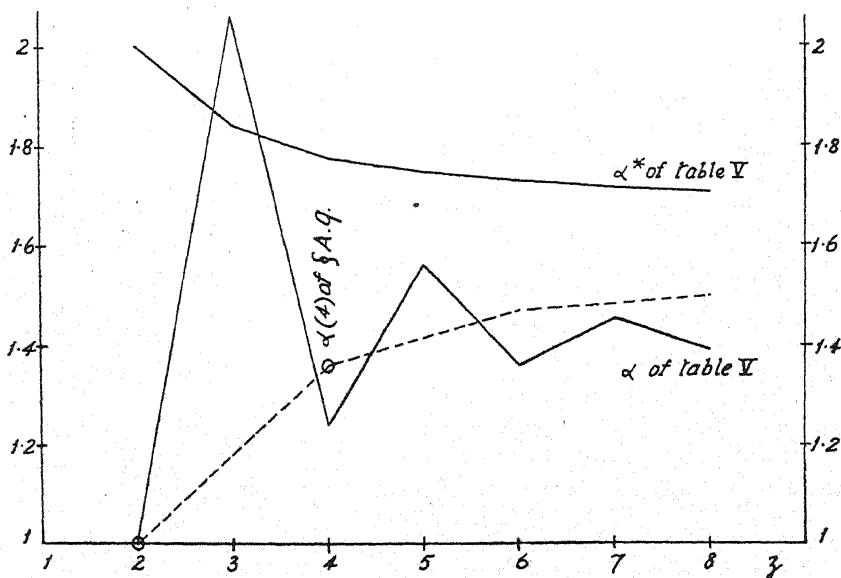
$$l(4) \doteq 0.925 \text{ so that } \alpha(4) \doteq 1.36.$$

Table II. does not provide us with sufficient data to enable us to make a similar calculation for a triangular array, and in any case the result would be of little use in an estimation of $l(6)$ since the triangular array is not a simple lattice (in the sense of § A. 7). But comparing the above value of $\alpha(4)$ with the corresponding ones of Table V. leads us to suppose (see Fig. 4 that $\alpha(6)$ and $\alpha(8)$ are fairly near the value 1.5.

TABLE VI.*

z .	μ_z .	μ_z^c .	$(\mu_z/\mu_z^c)^{\frac{1}{z}} = l_z$.
1	—	—	—
2	1.618	2.414	0.818
3	1.932	2.190	0.939
4	2.84	3.732	0.872
5	3.542	4.075	0.932
6	5.057	6.32	0.894
7	(6.54)	(7.54)	0.930
8	(9.07)	11.04	0.906

* () figures are found roughly by extrapolation from Table I.: we take $\lambda_7 = 1.71$; $\lambda_7^c = 1.78$; $\lambda_8 = 1.735$. l_7 and l_8 are very uncertain.*

FIG. 4.—Estimates of the factor α .

The dotted line is suggested as a possible indication of correct values of α .

A10. Conclusion.

From the studies of this appendix we feel justified in assuming that the molecular freedom λ for simple cubic packing of diatomic molecules is approximately 2.38 ($z''' = 4.76$) while for body centred cubic packing

it is possibly in the neighbourhood of 2.88. For both these lattices the value of α , though necessarily estimated by very indirect methods, seems to be about 1.5.

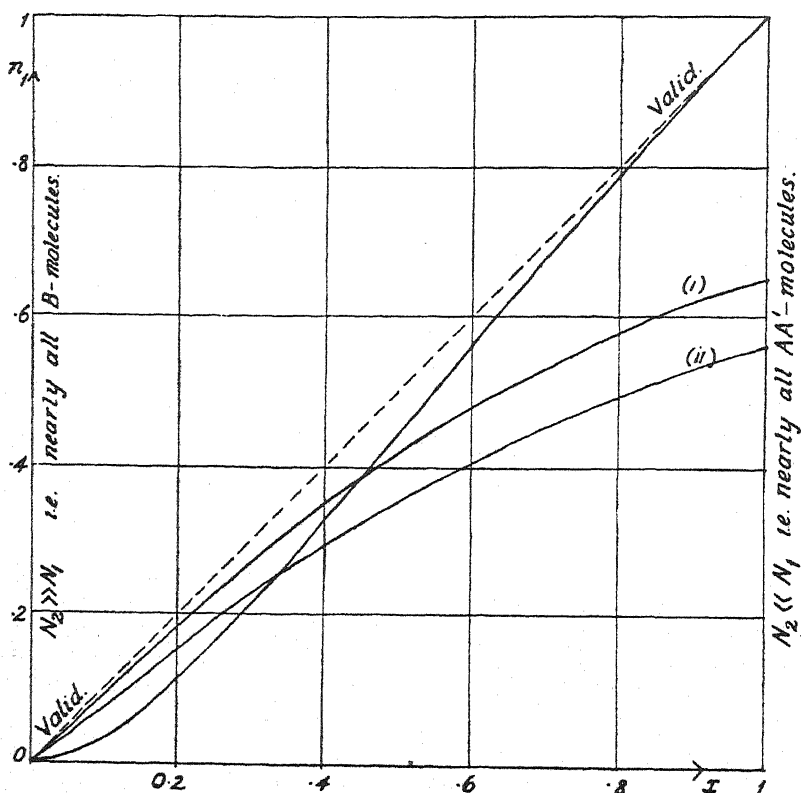


FIG. 5.—Partial vapour density of AA'-molecules for different values of the numerical constants.

The curves show

$$n_1 = (n_1')/(n_1')_0$$

$$\text{where } n_1' = (n_1')_0 \frac{z'''}{z} \frac{x}{1+x} \exp \left(\frac{z'(z-z'')}{z} \cdot \frac{x}{(1+x)^2} \right) \quad (x \ll 1)$$

$$= (n_1')_0 \left(\frac{2x}{1+x} \right)^2 \quad (1-x \ll 1)$$

$$(n_1')_0 = \frac{\sigma f_1'}{z''' v_1} e^{\epsilon_1/kT}.$$

$$(i) \quad z = 4, \quad z''' = 3.6, \quad \frac{z'(z-z'')}{2z} = \frac{3}{4}.$$

$$(ii) \quad z = 8, \quad z''' = 5.76, \quad \frac{z'(z-z'')}{2z} = \frac{7}{8}.$$

Figs. 5 and 6 show the changes in the vapour density curves (given by formulæ (25) and (28)) produced by ascribing different values to the lattice constants z, z'', α , etc. In each case $n_1'/(n_1')_0$ or $n_2'/(n_2')_0$ is plotted as a function of $x = N_1/(N_1 + N_2)$.

The curves (i) are drawn for $z = 4$, $z''' = 3.6$, $\frac{z'(z - z'')}{2z} = \frac{3}{4}$, and $\alpha = 1.36$, and refer strictly to a plane square array but also possibly to the three-dimensional diamond lattice; and the curves (ii) are drawn for $z = 8$, $z''' = 5.76$, $\frac{z'(z - z'')}{2z} = \frac{7}{8}$ and $\alpha = 1.5$ and refer to body

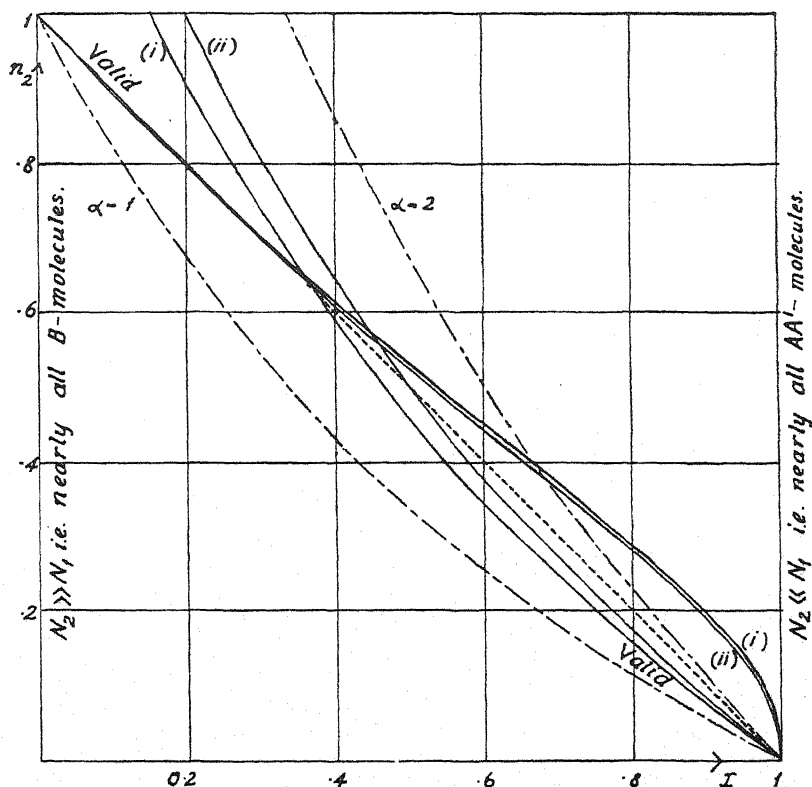


FIG. 6.—Partial vapour density of B-molecules for different values of the numerical constants.

The curves show

$$n_2 = n_2' / (n_2')_0$$

where
$$n_2' = (n_2')_0 \left(\frac{1-x}{1+x} \right)^{\frac{1}{2}} \exp \left\{ - \frac{z'(z-z'')}{2z} \frac{x^2}{(1+x)^2} \right\} \quad (x \ll 1)$$

$$= (n_2')_0 \frac{1-x}{1+x} \cdot \alpha \quad (1-x \ll 1)$$

and
$$(n_2')_0 = \frac{f_2'}{v_2} e^{\epsilon_2/kT}.$$

(i) and (ii) as in Fig. 5.

For (i) we have taken $\alpha = 1.36$,

and for (ii) $\alpha = 1.5$.

centred cubic packing. They should be compared with the curves of Fig. 1 which appertain to simple cubic packing.

The general features of the curves are the same in each case. It will be seen that values of α close to 1.5—as suggested by § A. 9—are the

only ones for which we can reasonably pass from the curves (25) to the curves (28) in accord with equation (29).

The curves in Fig. 1 are drawn for $z = 6$, $z''' = 4.76$, $\frac{z'(z - z'')}{2z} = \frac{5}{6}$, $\alpha = 1.5$. The continuous smoothed curves there shown satisfy equation (29) for all values of x and run into the broken curves at the ends at which these curves are valid approximations. The continuous curves embody to the best of our judgment the most probable result of the investigation.

EQUILIBRIUM AND KINETIC STUDIES ON REACTIONS OF THE MENSCHUTKIN TYPE IN DILUTE SOLUTION. PART I. SUGGESTED EXPLANATION OF THE SOLVENT EFFECT.

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The velocity constant, k , of a bimolecular reaction may be represented by the well-known expression, $k = PZe^{-E/RT}$, where the product $Ze^{-E/RT}$ gives the activated collision frequency; if all activated collisions are fruitful P will be approximately unity and the reactions are termed "normal." This obtains in most gaseous reactions and also for a large number of reactions in solution.¹ But there are many reactions for which the value of P is very much less than unity and of the order of 10^{-4} to 10^{-9} . Such reactions are termed "slow reactions" and no adequate explanation of them on the kinetic-collision theory has been advanced. A typical "slow reaction" is the association of a tertiary base with an alkyl halide to give a quaternary salt (Menschutkin reaction). It has been observed that all reactions of this particular type are subject to a marked solvent effect.² In the course of a general investigation of the association of dimethylaniline and methyl iodide the influence of solvent has been studied and the results discussed in this paper seem to lead to a clarification of ideas regarding this effect.

Purification of Materials.

Methyl iodide was purified by washing successively with dilute sodium thiosulphate, water, dilute sodium carbonate, and again with water several times. After drying over calcium chloride it was distilled, $n_D^{20} = 1.5300$.

Dimethylaniline was refluxed for twenty-four hours with "Analar" acetic anhydride and fractionally distilled. The dimethylaniline thus obtained was treated successively with sodium hydroxide, and water, dried over caustic potash and fractionated, $n_D^{20} = 1.5578$. The purified product was quite stable and gave no coloured compounds with methyl iodide.³

Benzene.—Technical "crystallisable" benzene was freed from thiophene by shaking with concentrated sulphuric acid.⁴ After washing with water and sodium carbonate it was dried with calcium chloride and with sodium,

¹ Moelwyn-Hughes, *Kinetics of Reactions in Solution*, 1935, p. 79.

² Menschutkin, *Z. physik. Chem.*, 1890, 6, 41.

³ Williams and Perrin, *Proc. Roy. Soc., A*, 1937, 159, 162.

⁴ Roberts and Bury, *J. Chem. Soc.*, 1923, 123, 2037; Barnes and Fulweiler, *J. Amer. Chem. Soc.*, 1929, 51, 1750.

distilled, and the middle fraction of the distillate fractionally crystallised. F.P. = 5.54° ; $n_D^{20} = 1.1016$.

Ethyl Acetate.—The commercial product was washed several times with water, shaken with calcium chloride and fractionally distilled. B.P. $76.1-76.5^{\circ}/768$ mm.; $n_D^{20} = 1.3725$.

Acetone was purified by the method of Bramley⁵ and boiled at $55.9-56.0^{\circ}/748$ mm.; $n_D^{20} = 1.3589$.

Nitrobenzene.—Commercial nitrobenzene was shaken vigorously with several quantities of concentrated sodium hydroxide, washed successively with water, 50 per cent. hydrochloric acid, and again with water, dried over calcium chloride, distilled, and fractionally crystallised twice. F.P. = 5.82° ; $n_D^{20} = 1.5524$.

Methyl Alcohol.—Commercial methyl alcohol was purified by the method of Bjerrum and Zechmeister.⁶

B.P. = $64.20-64.30^{\circ}/754-758$ mm.; $n_D^{20} = 1.3291$.

Experimental Procedure.

The reaction has been studied by the original method of Menshutkin² using glass bulbs or tubes of about 11 c.c. capacity in preference to other methods adopted in the study of such reactions.⁷⁻¹⁰

The actual procedure in the present investigation was to weigh out the reactants in thin-walled glass tubes of from 0.05 to 0.5 c.c. capacity. The bulb containing the methyl iodide was broken under a small quantity of solvent (ca. 2 c.c.) in a 100 c.c. standard flask to prevent loss by evaporation. About 50 c.c. of solvent were added. The amine bulb was broken under solvent in another vessel and added to the iodide solution and the vessel thoroughly washed out with more solvent. The volume was made up to the graduation mark, the temperature being noted in order to make the necessary correction for expansion and enable all concentrations to be compared with the concentration at 15° .

Samples of the solution (10 c.c.) were introduced into the reaction vessel, previously thoroughly washed and dried out with a current of hot air. The tubes were sealed off and placed for the desired time in electrically-heated, oil-covered water thermostats, incorporating a toluene regulator and giving satisfactory temperature control to 0.1° up to 90° . All temperatures were measured by thermometers graduated in one-tenths and checked against N.P.L. certificate thermometers.

There are several obvious advantages in the procedure used in this work. The solutions are all measured out at room temperature and therefore there is no need for a correction for the expansion of the volumetric apparatus nor for the evaporation of the solvent, factors of the greatest importance at the higher temperatures. Moreover, by this method the reaction can be studied at temperatures considerably above the boiling-point of the solvent if care is exercised. (Actually tubes of the reaction mixture in acetone have been heated to 150° in oil thermostats). Further, since in dilute solution at room temperature the reaction is extremely slow, the amount of salt formed during the preparation of the tubes is negligibly small. Experiments conducted in acetone at 12° with 0.01 molar concentration of each reactant confirm this.

The reaction was stopped after the desired time by quenching the tube in cold water, and extraction of the salt was completed within thirty minutes.

⁵ Bramley, *J. Chem. Soc.*, 1916, 109, 10.

⁶ Bjerrum and Zechmeister, *Ber.*, 1923, 56, 894.

⁷ Essex and Gelormini, *J. Amer. Chem. Soc.*, 1926, 48, 882.

⁸ Davies and Lewis, *J. Chem. Soc.*, 1934, 1599.

⁹ Gladischew and Syrkin, *Acta Phys. Chem., U.R.S.S.*, 1935, 2, 291.

¹⁰ Gibson, Fawcett and Perrin, *Proc. Roy. Soc., A*, 1935, 150, 223.

The rate of the reaction has been followed by estimating the iodide ion concentration in the solution after any particular time.^{2, 7, 8, 11, 12} Owing to the dilute solutions used the gravimetric and volumetric methods previously employed were unsuitable and the estimation has been carried out electrometrically. The iodide was first of all extracted from the reaction mixture by addition of 30 c.c. benzene followed by three separate 10 c.c. quantities of water. The aqueous extract is passed through a wet filter paper to remove droplets of oil,⁷ and is either titrated directly with silver nitrate (0.001-0.0005 M) or, if there is a high concentration of iodide ions, the solution is diluted and aliquot portions titrated. In the actual titrations a rotating silver electrode, which acts as an efficient stirrer, is connected through an agar-agar-barium nitrate bridge with a quinhydrone reference electrode. Crystals of "Analar" barium nitrate are added to preserve the conductivity in the very dilute iodide solution. The barium nitrate serves, in addition, in hastening the coagulation of the silver iodide at the equivalence point.¹³ This method has been used successfully for some eighteen months in this work and its eminent suitability and accuracy is unquestionable, especially in the light of the recent work of Kolthoff and Lingane¹⁴ on the potentiometric titration of very dilute solutions of silver nitrate and potassium iodide. The silver nitrate was added rapidly until near the equivalence point when the e.m.f. of the cell was noted after the addition of each drop, sufficient time (about 3 mins.) being allowed for the electrode to come to equilibrium with the solution. The equivalence point was found by extrapolation and was taken as the point of maximum inflexion in the $\Delta E/\Delta V$ curve. The performance of the electrode is greatly improved by excluding light from the titration vessel.

Previous to adopting this method of estimation attempts were made to estimate the iodide electrometrically, using a mercury electrode and mercuric chloride as titrant,¹⁵ but this was abandoned on account of the precipitation of complex mercury salts which vitiated the equivalence point.

Owing to the very favourable distribution ratio of quaternary salt between benzene and water it is possible to obtain titres on the same solution consistent to within one drop.

The equilibrium value of the iodide ion concentration was considered to have been attained when three tubes gave the same titre after being maintained at a particular temperature for different periods of time. The value of K derived in this manner has been checked, wherever possible, by the attainment of equilibrium by dissociation.

Experimental Results and Discussion.

The influence of solvent on the rate of formation of quaternary ammonium salts was observed, as has been mentioned, by Menschutkin forty-seven years ago. He records that in acetophenone and in benzyl alcohol the rate is some 700 times greater than in hexane. Similar observations have been made by other workers in this field and various theories have been propounded to explain this effect. It must be pointed out, however, at the outset, that previous observations, as far as can be ascertained, have been made at reactant concentrations considerably greater than those used in this investigation; and, further, that none of these explanations is completely satisfactory.

A fact which so far seems to have been overlooked is that for all "slow reactions" showing a marked solvent effect measurements have

¹¹ Winkler and Hinshelwood, *J. Chem. Soc.*, 1935, 1147.

¹² Grimm, Ruf and Wolff, *Z. physik. Chem., B*, 13, 301.

¹³ Kolthoff and Furman, *Potentiometric Titrations*, 1926, p. 166.

¹⁴ Kolthoff and Lingane, *J. Amer. Chem. Soc.*, 1936, 58, 1524, 3457.

¹⁵ Ref. 13, p. 186.

been made (at least in the "non-polar" solvents) on reactions which are not completely homogeneous. For instance, in the literature on Menshutkin reactions the recorded concentrations are such that the product (the quaternary salt) must almost certainly have separated out during the course of the reaction. The effect of the reaction product depositing as a separate phase will only be relatively unimportant if the reaction goes to completion in the *true homogeneous phase* and if the effect of the reverse reaction is *negligible*. The possibility of an appreciable reverse reaction has hitherto been tacitly assumed or completely neglected.

A typical reaction of the Menshutkin type, *viz.*, the interaction between dimethylaniline and methyl iodide, has been examined to determine whether such a reverse reaction does exist and, if so, to what extent. It has been found that the equilibria in "non-polar" and relatively "non-polar" solvents, in a homogeneous system, lie practically on the side of complete dissociation, indicating that the dissociation reaction is of considerable importance. The observed rate thus appears to depend on the following factors:—

(a) The rate of the true bimolecular association. The primary product of such an association will be a salt molecule in the *dissolved state* which, in "non-polar" solvents, has only a transient existence in this state (a "*nascent*" molecule).^{*} This primary process will take place in all solutions irrespective of initial reactant concentrations. But when relatively high concentrations of reactants are used salt crystals are deposited largely because of their low solubility in the "non-polar" solvents. The non-deposition of crystals from dilute solutions has been judged as the criterion that only "nascent" molecules are formed. It has been found (*vide* Table I.) that in a benzene solution at 65°, $m/25$ with respect to both reactants, the equilibrium concentration of "nascent" molecules is approximately of the order of the solubility saturation limit of the salt, s . For a more concentrated solution, say $m/2$, the rate of formation of "nascent" molecules is 156 times that in the $m/25$ solution and therefore the extent of supersaturation cannot exceed 156 s ; but this quantity is negligibly small compared with the amount of salt which crystallises out and which is practically completely responsible for the measured titre.

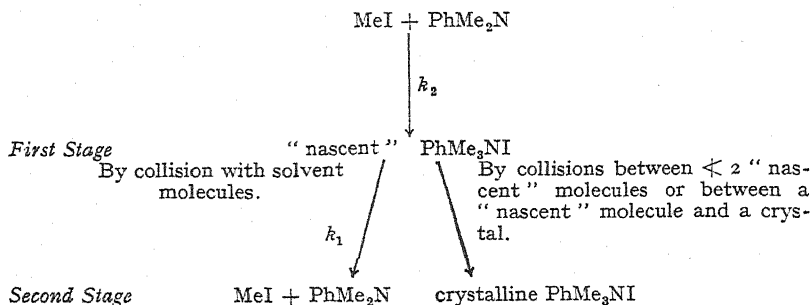
(b) The second stage consists in the removal of these "nascent" molecules from the reaction phase, since, as has been shown in the preceding paragraph, these do not tend to accumulate in significant quantities.

It is necessary at this stage to define the significance of certain terms which will be employed in the subsequent discussion. A reaction of the type under discussion cannot be regarded as a homogeneous reaction to which the ordinary laws apply *directly*. Moreover, since the reaction does not proceed at the division of phases, it cannot be regarded as a

^{*} The term "nascent" molecule is used to save repetition of the much longer and more unwieldy term "a dissolved salt molecule which is unsolvated and unstable." In "non-polar" solvents solvation of salt molecules does not occur, and all dissolved salt molecules will be "nascent." On the other hand, when the salt is dissolved in a "polar" solvent solvation occurs and this renders the dissolved molecule more stable; but at the same time there will be varying amounts of unsolvated molecules depending on the solvent employed. Accordingly, in "polar" solvents the proportion of dissolved molecules which are "nascent" will be greatly diminished. It must be emphasised that, since there is no difference in the properties of "nascent" and "ordinary" molecules, the term "nascent" molecule must not be taken to connote such terms as "intermediate complex," "activated complex," etc.

heterogeneous reaction. In order to obviate any confusion in the ensuing discussion the term "quasi-homogeneous" will be used to indicate a reaction which proceeds between molecules in a *particular phase* to give molecules of the product having a definite life-period in the *same phase*, although *some* molecules may eventually appear in a *different phase*. The term homogeneous reaction will be reserved to describe a reaction proceeding in a particular phase to give a product uniformly dispersed in the same phase.

The effect of an appreciable reverse reaction can best be illustrated by comparing the theoretical rate of formation of "nascent" molecules with the speed of their removal from the liquid phase. This may proceed according to the following mechanism:—



Two processes are thus seen to be operative in the removal of the "nascent" molecules from the reaction phase:

(i) A dissociation process due to collisions of critical violence with solvent molecules, the rate of which is given by the expression k_1c , where c is the concentration of "nascent" molecules, and k_1 the unimolecular dissociation constant.

(ii) If the concentration of "nascent" molecules is sufficiently high they may become stabilised by entry into the crystal lattice at a rate which will be given by the expression, $f_x(c-s)$, in which $(c-s)$ is the extent of supersaturation, and f_x is a function of the velocity of crystallisation.

These two processes account for all the "nascent" molecules formed by the primary reaction and so the total effect may be equated to the theoretical speed of their formation; thus,

$$k_2[\text{MeI}][\text{PhMe}_2\text{N}] = f_x(c-s) + k_1c \quad \quad \quad (i)$$

If salt crystals are present from the beginning of the reaction, as is always the case when fairly high initial concentrations of reactants are employed, as for instance M/10, the *observed* rate obtained by measuring the rate of salt formation will depend entirely on the rate of the crystallisation process, given by $f_x(c-s)$. For this term we may now write $k_{2(\text{obs.})}[\text{MeI}][\text{PhMe}_2\text{N}]$ and substituting in equation (i) we get

$$k_{2(\text{obs.})}[\text{MeI}][\text{PhMe}_2\text{N}] = k_2[\text{MeI}][\text{PhMe}_2\text{N}] - k_1c \quad \quad \quad (ii)$$

But the equilibrium constant, $K = k_1/k_2$,
and therefore

$$k_{2(\text{obs.})} = k_2 \left(1 - \frac{Kc}{[\text{MeI}][\text{PhMe}_2\text{N}]} \right) \quad \quad \quad (iii)$$

* The term $\pm dc/dt$ has been omitted from the right hand side of this equation, since its magnitude is negligible.

It will be shown that K may have large values in solvents of "low polarity" and so the expression $Kc/[\text{MeI}][\text{PhMe}_2\text{N}]$ may have a value approaching, but never exceeding, unity. Thus, at any given instant, $k_{2(\text{obs.})}$ differs appreciably from the true rate coefficient of the association process and is therefore fictitious. In the absence of more detailed knowledge of the mechanism of the crystallisation process it is not possible to extend further the theoretical derivation of $k_{2(\text{obs.})}$ so as to explain the sensibly constant results which have been obtained by other workers. It seems probable, however, that these results have been obtained through insufficient variation of experimental conditions. With the more sensitive methods which have been used in the present investigation serious departures from the normal bimolecular course are revealed.

Most of the published work on reactions of the Menshutkin type refers to measurements on solutions usually approximately $M/10$ or stronger and seldom followed beyond the stage of half completion. Under these conditions the velocity constant evaluated by means of the usual expression,

$$k_{2(\text{obs.})} = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)},$$

has tolerably constant values. This is found to be approximately true for the present reaction also, using concentrations of the order indicated above. It must be remembered, however, that this expression gives an *average* value for the velocity coefficient from zero time up to the time of observation and does not give therefore a true indication of the value of the rate coefficient at any given instant. The difference formula, *viz.*,

$$k'_{2(\text{obs.})} = k_{2(\text{obs.})} t_1 \rightarrow t_2 = \frac{2.303}{(t_2 - t_1)(a-b)} \log \frac{(a-x_2)(b-x_1)}{(b-x_2)(a-x_1)} \quad (\text{iv})$$

should always be used to obtain a truer indication of the instantaneous rate coefficient if the results are of sufficient precision to justify its application.

The present reaction has been studied, chiefly in benzene at 65° , over a wide range of initial concentrations, and considerable diversity of behaviour has been observed. The results, summarised in Table I., show that the reaction does not proceed at initial concentrations less than $M/25$. Presumably under these conditions the system comes to an equilibrium so near complete dissociation that it is impossible to detect any salt formation, even with the sensitive electrometric method

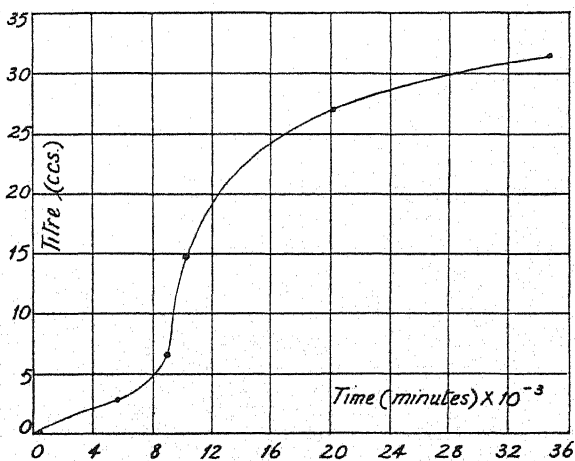


FIG. 1.—Solution V.

comes to an equilibrium so near complete dissociation that it is impossible to detect any salt formation, even with the sensitive electrometric method

TABLE I.

No. of Soln.	Conc. of Reactants (g.-mols./litre).		Temp. °C.	No. of Tubes.	Remarks.
	MeI.	PhMe ₂ N.			
I.	0.00183	0.00162	12	9	No crystals deposited up to 8 days. All titres <0.05 c.c., 0.00073M AgNO ₃ . If reaction had gone to completion titre would have been about 25 c.c.
			30	9	
			60	6	
II.	0.0140	0.0117	12	3	Salt not detected after 2 days at 65° nor after 14 days at 12° and 45°.
			45	4	
			65	2	
III.	0.0567	0.0494	12	4	Salt separated out after a short time in all except one tube at 12° (see discussion).
			30	5	
IV.	0.0482	0.1176	12	5	2 tubes of silica. Crystals deposited within a few hours. Titres for glass and silica tubes of the same order after 9 and 15 days.
V.	0.0410	0.0517	16	1	Values for velocity const. show considerable drift. The tube at 16° gave much bigger titre than tube at 65° after the same time. (See Table II.)
			65	8	
VI.	0.1052	0.0836	65	9	} k_2 (obs.) subject to marked fluctuation (see Fig. 2).
VII.	0.0971	0.0953	65	9	
VIII.	0.0823	0.0904	65	7	
IX.	0.1237	0.0869	65	8	
X.	0.0932	0.1187	65	9	In presence of powdered glass. See Table III. and Figs. 3 and 4. k_2 (obs.) average = 7.19×10^{-4} .

of estimation employed. At initial concentrations of the order of M/20 the reaction proceeds extremely slowly and the titration curve is typical of reactions showing an induction or marked auto-catalytic effect. The titres obtained with one such benzene solution at 65° are shown numerically in Table II. and graphically in Fig. 1.

Apparently, therefore, in solutions of this initial concentration the reaction proceeds more rapidly at the lower temperature and this may be tentatively assumed to be due to the diminished solubility and decreased rate of dissociation of "nascent" molecules.

Compared with the rate of the reaction at M/10 initial concentration the rate in M/20 solution is far less than can be accounted for by the diminished concentrations.

When the reaction proceeds smoothly, the titration curves for M/10 solutions follow roughly the same pattern as for the M/20 solutions, and the initial induction period, though much reduced in comparison with the total range of the reaction, is still easily observable. Reference to Fig. 2 will show that for different solutions (VI.-IX.) this initial induction period

TABLE II.

Time (mins.) . .	525	1960	5670	8940	10,200	20,160	34,740
Titre (c.c. of 0.0005937M AgNO ₃)	0.20	*	2.80	6.54	14.75	26.93	31.51
$k_2(\text{obs.}) \times 10^5$. .			1.12	2.17	4.43	3.84	2.67

Average $k_2(\text{obs.}) = 2.84 \times 10^{-5}$ gm.-mols. per litre per minute.

The initial concentrations of reactants were, $[\text{MeI}] = 0.0410$ and

$[\text{PhMe}_2\text{N}] = 0.0517$ gms. per litre,

and therefore if the reaction had gone to completion the final titre should have been 683 c.c.

* On removal from the thermostat this tube contained no crystals; it was kept at room temperature and after a further 13 days (in all 20,580 minutes) gave a titre of 68.2 c.c. (Cf. titre for tube removed after 20,160 minutes.) Another tube kept wholly at room temperature for 10,200 minutes gave a titre of 29.5 c.c., compared with a titre of 14.75 c.c. for a tube kept at 65° for the same period.

is covered in different times and the readings corresponding with points on the steep upward portion of the curve are very erratic. Thus, with solution IX., one tube contained a considerable quantity of "woolly" crystals, whilst the others contained much smaller amounts of crystals adhering, for the most part, to the sides of the tubes. The first tube was examined along with one of the others after an equal time and they gave titres of 173.8 and 39.35 c.c. respectively. The effect seems to be due to the relative ease of precipitation of the solid product in the different reaction tubes. Since some crystals are present in all the tubes practically from the commencement of the reaction the effect cannot be due to "seeding" in the ordinary sense. After covering the initial induction period the reaction follows an apparently bimolecular course for about a 25 per cent. range (M/10 solution), then a rapid falling off of the velocity constant occurs and the reaction eventually comes to an equilibrium instead of proceeding to completion. Similar cases of anomalous or erratic bimolecular velocity constants have already been reported by Moelwyn-Hughes and Hinshelwood.¹⁶ Quite recently Davies and Cox¹⁷ have investigated in chloroform solution the reaction under consideration in this paper and from their published data there appears to be no indication of an induction effect but the reaction velocity coefficients do show a decided drift.

In ethyl acetate solutions at 12°, with initial concentrations of approximately M/10, the values of $k_2(\text{obs.})$ are tolerably constant (Table III.)

TABLE III.

Time (mins.)	105	265	450	1145	1315	1520	2595	3130	4035
Titre c.c. of 0.000635 M AgNO ₃ .	13.96	29.32	45.80	104.24	119.5	138.0	221.5	262.5	319.0
$k_2(\text{obs.}) \times 10^4$	4.55	3.88	3.66	3.49	3.53	3.75	3.77	3.68	3.42

Average $k_2(\text{obs.}) = 3.64 \times 10^{-4}$ gm.-mols. per litre per minute.

The initial concentrations were $[\text{MeI}] = 0.1005$ and $[\text{PhMe}_2\text{N}] = 0.1732$ gm.-mols. per litre, and therefore if the reaction had gone to completion the final titre should have been 1582 c.c.

¹⁶ Moelwyn-Hughes and Hinshelwood, *J. Chem. Soc.*, 1932, 231.

¹⁷ Davies and Cox, *ibid.*, 1937, 614.

but observations cover only the initial one-third of the reaction and the drift due to the reverse reaction is therefore not observed.

Reaction in Benzene in the Presence of Powdered Glass.

A possible explanation of the erratic titres obtained for the reaction in benzene is the variation in the relative ease of crystallisation in dif-

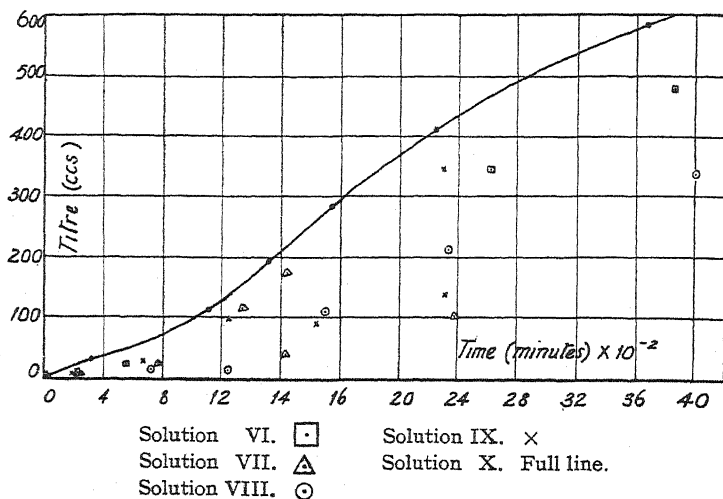


FIG. 2.

ferent tubes, *i.e.*, the "seeding" properties of a tube play an important rôle. To test this view the reaction in benzene (M/10) was re-investigated with about 0.2 gm. of finely powdered glass added to each tube to facilitate "seeding." Under these conditions a smooth curve showing

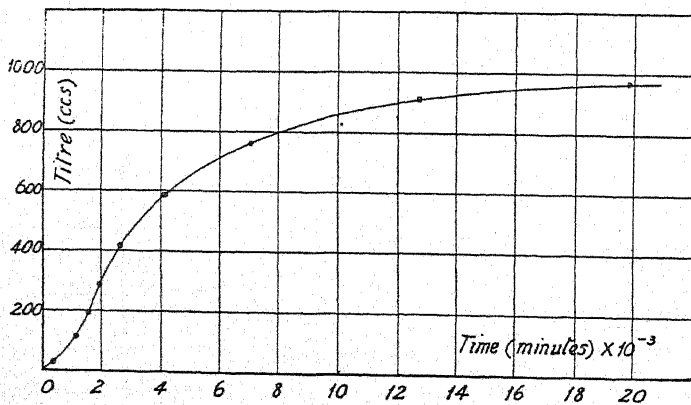


FIG. 3.—Solution X.

an induction effect (Figs. 2 and 3, solution X) was obtained when the titres were plotted against time. This observation and the shape of the other curves in Fig. 2 lead to the conclusion that the crystallisation process is a major factor in determining the speed of the reaction.

When the bimolecular constant, $k'_{2(\text{obs.})}$, evaluated from equation (iv), was plotted against time the curve (Fig. 4) showed that $k'_{2(\text{obs.})}$ at first increases rapidly and after passing through a maximum at about 2300 minutes falls off slowly with time. The existence of this maximum value for $k'_{2(\text{obs.})}$ is quite consistent with the suggested mechanism

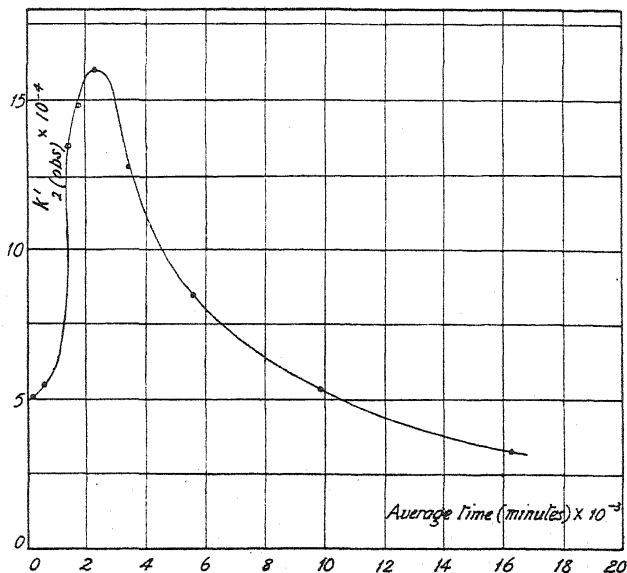


FIG. 4.—Solution X. Variations of $k'_{2(\text{obs.})}$ at 65.0°.

and corresponds, presumably, with the conditions of maximum supersaturation which will be attained after a certain definite time, depending on the particular initial concentrations employed. Unfortunately it is impossible to predict the time required to reach maximum supersaturation owing to lack of definite information regarding f_w (see equation (i)).

Equilibria in Systems of Mixed Phases.

The scheme outlined for a "quasi-homogeneous" reaction postulates that the reaction system will come to an equilibrium when the concentration of "nascent" molecules, c , is equal to their saturation solubility limit, s , in the reaction mixture. But s has a constant value, and is attained only when the rate at which salt is formed equals the rate at which it dissociates, *viz.*, k_1s . Accordingly, the rate of formation, and hence the product $[\text{MeI}][\text{PhMe}_2\text{N}]$, should be a constant in any system which has come to equilibrium with crystalline salt, provided that the differences in the various possible combinations of equilibrium concentrations of the two reactants are not so great as appreciably to alter the solubility of "nascent" salt in the corresponding equilibrium media. To test this is rather difficult, because of the time taken to reach equilibrium. An approximate test is obtained by extrapolating the equilibrium titration value from appropriate titration curves and computing the corresponding iodide ion concentration. By subtracting this value from the initial concentration of each reactant the equilibrium concentrations

are obtained. The equilibrium titre cannot be extrapolated with great accuracy, but an error of even several cubic centimetres does not introduce a substantial divergence in the value of the equilibrium concentration product, as is shown in Table IV., which contains the results of this calculation for solutions V., VI., IX. and X. ($[]_i$ and $[]_e$ represent respectively initial and equilibrium concentrations in gm.-mols. per litre.)

TABLE IV.

Soln.	$[MeI]_i$	$[PhMe_2N]_i$	Estd. Equil. Titre.	$[I]_e$	$[MeI]_e$	$[PhMe_2N]_e$	$\frac{[MeI]_e}{[PhMe_2N]_e}$
V.	0.0410	0.0517	35	0.0027	0.0383	0.0496	0.00193
			40	0.0024	0.0386	0.0493	0.00190
			45	0.0021	0.0389	0.0490	0.00187
VI.	0.1052	0.0836	850	0.0505	0.0547	0.0331	0.00181
			855	0.0508	0.0544	0.0328	0.00178
			900	0.0535	0.0517	0.0301	0.00156
IX.	0.1237	0.0869	950	0.0565	0.0672	0.0304	0.00204
X.	0.0932	0.1187	1000	0.0594	0.0338	0.0593	0.00200

These results show that the equilibrium concentration product is practically constant and of appreciable magnitude, and, therefore, supports the contention that the dissolved salt, in spite of its minute concentration, plays an important part in determining the rate of the reaction.

Influence of Solvent on the Equilibrium Constant.

From the nature of $k_{2(obs.)}$ the value of the critical increment, calculated from the temperature variation of this term, will be lower than the true value for the homogeneous bimolecular process, since, in all but the very "polar" solvents, the speed of dissociation and the saturation solubility will be greater at the higher temperatures. The discrepancy between $k_{2(obs.)}$ and the true bimolecular constant may be sufficient to account not only for the marked solvent effect, but also possibly for the slowness of the reactions. The original comparison of reaction rates in various solvents was made by Menschutkin² at 100°, where these effects would be more pronounced.

In establishing the generality of the proposed explanation, it is of interest to consider the variation in the values of the equilibrium constant, K , in different solvents; this is shown in Table V.

From these data it is clear that the solvent has a profound influence on the value of K . On a kinetic basis it is improbable that the rate of the association reaction undergoes substantial change in different media. Doubtless solvation effects exist, but these would tend to alter the speed in the polar solvents in a sense opposite to the observed variations.¹⁸ Therefore, the variations in K arise almost entirely from the effect of solvent on the rate of the dissociation process. On this view the salt is stable only in highly "polar" solvents (e.g., methyl alcohol and water)

¹⁸ Ref. 1, p. 112.

TABLE V.

Solvent.	Initial Conc'n. in gm.-mols./litre.		K_{450} .	Remarks.
	[MeI].	[PhMe ₂ N].		
Benzene . .	0.00183	0.00162	Very large.	
Ethyl Acetate .	0.00380	0.00389	0.085	
Acetone . .	0.00859	0.0114	0.00533	Same value obtained by dissociation reaction.
Nitrobenzene .			0.00757*	
Methyl Alcohol	0.0534	0.0747	0	Salt solution stable at 90°.

* From Essex and Gelormini⁷ at 50.4°. In the present investigation values of K for different initial concentrations in nitrobenzene show a marked dilution effect.

and becomes increasingly less stable as the "polarity" of the medium decreases.^{17, 19} If the reaction is carried out in the gaseous phase, the extent to which the association would be expected to occur homogeneously is very small and, accordingly, if any reaction does occur, it will proceed principally by a heterogeneous mechanism. This, in fact, finds experimental verification in the observation of Moelwyn-Hughes and Hinshelwood¹⁶ that the association of triethylamine and ethyl iodide in the gaseous phase "takes place at least partly on the surface of the glass."

There are several other recorded anomalies in the kinetics of reaction in solution which, it is suggested, are capable of interpretation by a mechanism similar to that used for solvent effects. For instance, Grant and Hinshelwood,²⁰ in studying the benzylation of aniline in several solvents, observed that the velocity constants showed a pronounced drift and a dilution effect, particularly in hexane. They remark "the question arises whether the low energy of activation in carbon tetrachloride may not be spurious, and, indeed, whether other 'abnormally slow' reactions may not have hidden diffusion mechanisms even when they appear to be ordinary bimolecular reactions. This is improbable, since not all the reactions of the slow type involve the precipitation of a solid product, and, moreover, the Arrhenius equation is sometimes obeyed quite well. Nevertheless, the results show the need for circumspection." The reference to "slow reactions" not involving a solid product applies, presumably, to the esterification reactions, but these do not show any marked solvent effect.²¹ Solvent effects of the same kind have also been observed²² for the reaction between pyridine and methyl iodide, and for the benzylation of *m*-nitraniline. The influence of solvent on the rate of the first reaction, attributed by the authors to auto-catalysis by the precipitated product, is apparently analogous to

¹⁹ Corran, *Trans. Faraday Soc.*, 1927, **23**, 605; von Halban, *Z. physik. Chem.*, 1911, **77**, 719; Wedekind, Paschke and Mayer, *Ber.*, 1911, **44**, 1406.

²⁰ Grant and Hinshelwood, *J. Chem. Soc.*, 1933, 1353.

²¹ Menshutkin, *Z. physik. Chem.*, 1887, **1**, 611; Soper and Williams, *J. Chem. Soc.*, 1931, 2297.

²² Pickles and Hinshelwood, *J. Chem. Soc.*, 1936, 1353.

what has been found for the association of methyl iodide and dimethylaniline, and should therefore, presumably, be capable of interpretation by an identical mechanism. On the other hand, the benzylation processes are much more complex; they involve simultaneous reactions, and are not governed by the simple bimolecular laws. It is thus thought to be inadvisable to speculate on the nature of the mechanisms which operate in these reactions until considerably more experimental data, especially for dilute solutions, have been determined.

In conclusion, during the formation of quaternary salts in "non-polar" media the reaction product separates out and is not dissociated; the reaction proceeds on account of the stabilisation of the product by the lattice forces of the crystal. For all reactions of the Menschutkin type, and for analogous reactions in which a solid product is precipitated, it seems likely that the suggested mechanism will hold. The application of this view to other "slow" reactions, which show anomalous behaviour with change of solvent, must await further experimental evidence.

Summary.

An electrometric method, capable of determining accurately small concentrations of iodide ion, has been used to investigate the system, methyl iodide + dimethylaniline \rightleftharpoons phenyltrimethyl-ammonium iodide in benzene, ethyl acetate, acetone, nitrobenzene and methyl alcohol, in order to ascertain the nature of the solvent effect. A mechanism requiring the primary formation of unstable salt molecules in the dissolved state ("nascent" molecules) is proposed. These "nascent" molecules are removed from the reaction phase either by dissociation to reactants or by crystallisation. The speed of salt formation is governed by the relative magnitude of the rates of dissociation and crystallisation. The observed rate coefficient for the salt formation ($k_{s(\text{obs.})}$) therefore differs from the true rate coefficient of the homogeneous association process and an equation relating these is derived. Values of $k_{s(\text{obs.})}$ for ten different initial concentrations of the reactants in benzene at 65° do not follow the bimolecular law and exhibit considerable fluctuation for any particular reaction. In the presence of powdered glass the reaction proceeds smoothly but still shows progressive variations from the bimolecular constant. The values of the equilibrium constant exhibit enormous variation with change of solvent and it is considered that this is due almost entirely to alteration in the rate of the dissociation process. From extrapolated values for the equilibrium titre in benzene in the presence of solid, the product of the reactant concentrations at equilibrium is constant and of appreciable magnitude.

I wish to express my sincere thanks to Professor F. G. Soper, now of Otago University, New Zealand, who suggested the problem, and who supervised it in its initial stages; to Dr. W. Rogie Angus for many helpful suggestions, and for very valuable assistance in the preparation of this paper; to Dr. A. E. Bradfield for helpful criticism; and to Professor J. L. Simonsen, F.R.S., for his interest in the work.

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A POSSIBLE EXPLANATION OF SOME ANOMALOUS ELECTRIC DIPOLE MOMENTS.

BY F. C. FRANK AND L. E. SUTTON.

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Numerous instances are now known of compounds appearing to be polar although, on well-established stereochemical principles, it would be anticipated that they would be non-polar. H. O. Jenkins¹ has cited many of them, and further examples have since been observed and have served to emphasise the general nature of the phenomenon; these latter include several more metallic acetylacetonates,² co-ordination compounds of palladium,³ platinum,⁴ and gold,⁵ all of which have apparent moments of 1-1.8 Debye units.

It is improbable that these moments are real, especially as some of the compounds concerned, such as *p*-benzoquinone⁶ and beryllium basic acetate,⁷ have been shown to possess a centre of symmetry in the crystal. It is also improbable that they are due to very large atom polarisations for the definitely known values of this quantity are up to 6 c.c.,^{8, 9} or 5 to 10 per cent. of the electron polarisation,¹⁰ whereas the anomalous polarisations referred to are from 8 to 68 c.c. They have all been observed in solution, and the most plausible explanation is therefore that they are due to solvent effects. This hypothesis is supported by the facts that whereas the mercuric halides are polar in dioxane solution,¹¹ they are non-polar in the vapour phase,¹² and that 1.4 dioxane is also slightly polar in benzene but not in the vapour.^{13, 14} From the variety of solutes and the insensitivity of the apparent moments to the nature of the solvent it is obviously very improbable that the effects are all due to specific solute-solvent interactions, although these may occasionally be contributory factors,* and that therefore there must be some general effect.

A number of solvent effects which may arise have been discussed, but with two exceptions, the Raman-Krishnan effect^{28, 29} and the Jenkins-Bauer effect, these would not affect the polarisation of a solute molecule which has the symmetry necessary for it itself to be non-polar. The first of these two effects does not account for the phenomena

¹ H. O. Jenkins, *J. Chem. Soc.*, 1936, 862.

² A. E. Finn, *private communication*.

³ F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1935, 1549.

⁴ K. A. Jensen, *Z. anorg. Chem.*, 1935, 226, 284.

⁵ A. Burawoy and C. S. Gibson, *J. Chem. Soc.*, 1934, 860; 1935, 219.

⁶ J. M. Robertson, *Proc. Roy. Soc., A*, 1935, 150, 106.

⁷ L. Pauling and J. Sherman, *Proc. Nat. Acad. Sci.*, 1934, 20, 336.

⁸ S. Sugden, *Trans. Faraday Soc.*, 1934, 30, 734.

⁹ H. O. Jenkins, *idem.*, 739.

¹⁰ L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1934, 1094; 1935, 971.

¹¹ W. J. Curran and H. H. Wenzke, *J. Amer. Chem. Soc.*, 1935, 57, 2162.

¹² H. Braune and R. Linke, *Z. physikal. Chem., B*, 1935, 31, 2.

¹³ E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 1933, 63.

¹⁴ C. H. Schwingel and E. W. Greene, *J. Amer. Chem. Soc.*, 1934, 56, 653.

* As in the case of iodine in benzene.¹⁵

¹⁵ H. Müller and H. Sack, *Physikal. Z.*, 1930, 31, 815.

which we are considering, since the abnormality in solution depends primarily upon the value of a function ψ of the solvent, which is zero for carbon tetrachloride and negative for heptane, *cyclo*-hexane, and benzene and so gives zero or negative effects in these common solvents. The magnitude of the second effect was not estimated *a priori* but seemed likely to be of the right order of magnitude.

Essentially we have to consider two independent electric fields; one the intense, inhomogeneous field of polar groups of the solute molecule, the other the weak, approximately homogeneous field applied for the purpose of measurement. They exist together in a medium which, by virtue of its molecular nature, varies in density both with time and place. These variations distort the fields and change the induced moments in the medium, while conversely the electric fields exert a control upon the density fluctuations. Its final analysis is no simple matter, but we may distinguish two parts of the total effect which, though small, may be significant in the case of molecules of zero or very small dipole moment. One of these, which has been discussed by H. O. Jenkins^{1, 16} and S. H. Bauer,¹⁷ is the following. The principal solvent effect in the case of a polar solute molecule is due to the moment induced in the medium by the solute dipole.^{18, 19} This is not constant in a discontinuous molecular medium, but is subject to fluctuations with the motion of molecules in the liquid. As a result, the instantaneous dipole moment of a symmetrical molecule, which is non-polar owing to its having balanced polar groups, differs from zero. Thus, a contribution to the orientation polarisation arises from this, provided that the life of a fluctuation is not short compared with the relaxation time of molecular orientation, and Jenkins and Bauer have shown that, starting with an expression for the total dipole moment which Higasi developed¹⁹ and applying the standard kinetic theory of fluctuations, the probability that a molecule has a moment μ , when μ_0 is the moment in the gas phase, is

$$P(\mu) = Ce^{-\alpha(\mu/\mu_0 - 1)^2/2T}$$

where C and α are constants characteristic of the solute molecule, whence it can further be shown that the apparent moment ${}_2\mu$ of a compound with two such dipoles balanced is ${}_2\mu = \mu_0\sqrt{T/\alpha}$, and that of one with three such groups balanced is ${}_3\mu = \mu_0\sqrt{3T/2\alpha}$. We shall return to consider the time limitation after considering the second part of the total effect.

If we consider the molecules of solvent near a polar solute molecule, we know that they have induced dipoles in them depending upon the moment of the permanent dipole, their distance from and orientation to it. If the system is placed in an electric field it will change so as to maintain a minimum of potential energy. Thus, if a field is applied to the system of Fig. 1, with a positive electrode on the left, solvent molecules such as A and C, which carry induced moments augmenting the total moment, will approach nearer to the solute molecule, while those such as B and D, which carry induced moments reducing the total moment, move further away or spend less time there; therefore, in addition to the processes of orientation and distortion polarisation as

¹⁶ H. O. Jenkins, *J. Chem. Soc.*, 1936, 910.

¹⁷ S. H. Bauer, *J. Chem. Physics*, 1936, 4, 458.

¹⁸ F. C. Frank, *Proc. Roy. Soc., A*, 1935, 152, 171.

¹⁹ K. Higasi, *Sc. Pap. I.P.C.R. Tokyo*, 1936, 28, 284.

ordinarily understood, there is an increase of the total moment in the direction of the field owing to the presence of the solvent. With the field reversed the reverse motions would occur, decreasing the total moment, and thereby algebraically increasing the moment in the direction of the field in this case also. The effect considered therefore increases the total polarisability whatever the orientation of the dipole groups relative to the field.

Exactly parallel changes can occur with a molecule which has two or more opposed and equal dipoles, and therefore is non-polar as a whole, only provided that the dipoles are sufficiently widely separated for their fields not to neutralise one another in all the space where solvent is. The changes around each dipole group being then independent, there is a positive solvent effect for the molecule as a whole. Moreover, such a molecule may appear to have an orientation polarisation, if the deformation polarisation is allowed for by taking the molecular refractivity, because the redistribution of solvent molecules would be unable to follow the relatively high frequency field due to visible light and consequently the molecular refractivity observed in solution should be unaffected by this solvent effect. Qualitatively then this process could explain the

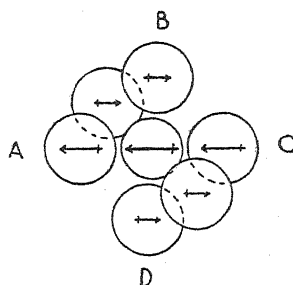


FIG. 1.—A possible explanation of some anomalous electric dipole moments.

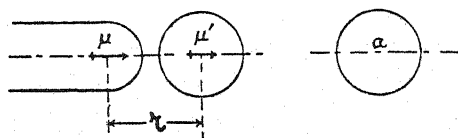


FIG. 2.—A possible explanation of some anomalous electric dipole moments.

Consider a solute molecule and a solvent molecule adjacent to and collinear with one of its polar groups (Fig. 2).

The induced moment in the solvent molecule is ¹⁸

$$\mu' = \frac{2\mu\alpha(\epsilon + 2)}{3r^3\epsilon}$$

where α is the polarisability of a solvent molecule, and ϵ is the dielectric constant of the medium. If the solute molecule is displaced a distance δr in the line of the dipole, there is produced a resultant moment change of

$$\frac{d\mu'}{dr}\delta r = -\frac{2\mu\alpha(\epsilon + 2)}{r^4\epsilon}\delta r \quad (1)$$

and the force exerted by the applied field F tending to displace solute molecules relative to solvent is

$$\frac{dV}{dr} = -\frac{F \cos \theta}{dr} \frac{d\mu'}{dr} = \frac{2\mu\alpha(\epsilon + 2)}{r^4\epsilon} F \cos \theta \quad (2)$$

θ being the angle of inclination of the field to the dipole axis.

We need an estimate of the restoring force opposing this displacement. For this purpose we may utilise the coefficient of adiabatic compressibility of the solvent, which is defined as

$$\beta = -\frac{1}{v} \left(\frac{dv}{dp} \right)_H$$

where p is the pressure applied to a volume v of the liquid. It is readily conceded that this is a loose way of estimating the restoring force, but none better presents itself, and no great accuracy is aimed at. We may consider that the increment of pressure δp accompanying a change in distance between molecules of δr arises from a Hook's Law force f between them, so that if a is the cross-sectional area of a molecule, and k is the force constant for a pair of molecules

$$a\delta p = f = k\delta r.$$

Since $dp = -\frac{1}{\beta v} dv = -\frac{3}{\beta r} dr$ we have that $f = -\frac{3a}{\beta r} dr$. Equating this to the electrostatic force dV/dr causing a movement δr we have

$$\frac{3a}{\beta r} \delta r = -\frac{2\mu\alpha(\epsilon + 2)}{r^4 \epsilon} F \cos \theta,$$

therefore
$$\delta r = -\frac{2\mu\alpha\beta(\epsilon + 2)}{3ar^3\epsilon} F \cos \theta,$$

and therefore from (1)

$$\delta\mu' = \frac{4\mu^2\alpha^2\beta(\epsilon + 2)^2}{3ar^7\epsilon^2} F \cos \theta.$$

The effective component of μ' is $\mu' \cos \theta$, whence

$$\frac{\mu'_{\text{eff.}}}{F} = \frac{4\mu^2\alpha^2\beta(\epsilon + 2)^2}{3ar^7\epsilon^2} \cos^2 \theta.$$

This "solvation polarisability" of a single molecule varies with θ , the angle between the field and the axis of the dipole, which is also the only axis of solvation polarisability of the molecule which we have so far considered, and therefore it would be expected that when a field is applied the solute molecule would orient in such a way as to increase the total polarisation still more. This it could do by decreasing the value of θ , i.e., by aligning its axis of maximum polarisability with the direction of the field. The mean moment in an assemblage of such solute-solvent systems is therefore obtained by applying the Boltzmann distribution equation, which gives the expression²⁰

$$\delta\bar{\mu}' = \frac{\int_0^\pi A e^{(\delta\mu' F \cos \theta)/kT} \delta\mu' \cos^2 \theta d\Omega}{\int_0^\pi A e^{(\delta\mu' F \cos \theta)/kT} d\Omega}.$$

If we write $\mu' = pF \cos \theta$, and $\cos \theta = \xi$ then, since $d\Omega = 2\pi \sin \theta d\theta$ for this problem, the above expression reduces to

$$\delta\bar{\mu}' = \frac{\int_{-1}^{+1} e^{(pF^2/kT)\xi^2} F \xi^2 d\xi}{\int_{-1}^{+1} e^{(pF^2/kT)\xi^2} d\xi}.$$

²⁰ P. Debye, *Polar Molekeln*, Leipzig, 1929, p. 25.

This can be integrated by series and gives

$$\frac{\delta\bar{\mu}'}{F} = p\left(\frac{1}{3} + \frac{4}{45} \frac{pF^2}{kT} + \dots\right).$$

Now $\frac{pF^2}{kT} = \frac{4\mu^2\alpha^2\beta(\epsilon+2)^2}{3ar^7\epsilon^2} \frac{F^2}{kT}$ is small compared with unity for ordinary field strengths at room temperatures, and hence

$$\bar{\alpha}_s = \frac{4\mu^2\alpha^2\beta(\epsilon+2)^2}{3 \cdot 3ar^7\epsilon^2}.$$

Thus the solvation polarisability is not an explicit function of temperature.

For $\mu = 2.5 \times 10^{-18}$ e.s.u., $\alpha = 10^{-23}$ e.s.u., $\beta = 6.6 \times 10^{-11}$ cm.² dyne⁻¹, $a = 10$ sq. Å, $r = 4$ Å, and $\epsilon = 2.3$, the value calculated for $\bar{\alpha}_s$ is 0.39×10^{-24} e.s.u., corresponding to a molecular polarisation $4\pi N\bar{\alpha}_s/3$ of 1 c.c.

This is the solvent effect upon polarisability for *one* solvent molecule near and collinear with *one* dipole group. It may readily be shown by a similar treatment to the above that the contribution of one solvent molecule in the zone perpendicular to the dipole axis is

$$\bar{\alpha}_s = \frac{\mu^2\alpha^2\beta(\epsilon+2)^2}{9ar^7\epsilon^2},$$

and so if we consider the effect of four such molecules, and if further we assume r to be the same as for the collinear solvent molecule, these double the total solvent effect.

In the foregoing discussion the solvation polarisability has been assumed to have a non-zero value along one axis only relative to the dipole, but this is because the model used is a crude one in which only collinear and zonal solvent molecules are taken into account, and in these the induced moments are parallel to the dipole axis. There must actually, however, be induced moments in molecules occupying intermediate positions, and these have components perpendicular to the dipole axis. By applying the same type of qualitative reasoning as before, it can be seen that there are also solvation polarisabilities in two directions perpendicular to the dipole axis and to one another. The solute-solvent system thus has, in general, three different polarisabilities along mutually perpendicular axes, α_{s1} , α_{s2} and α_{s3} . For an assemblage of such systems the effective polarisability for any axis is, as shown above, one third of the maximum value, *i.e.*, $\bar{\alpha}_{s1} = \alpha_{s1}/3$, and the total mean polarisability per polar group is therefore $\bar{\alpha}_s = (\alpha_{s1} + \alpha_{s2} + \alpha_{s3})/3$. This is exactly parallel to the result for a molecule which is anisotropic in its ordinary electron polarisability,²¹ and it follows quite simply that the solvation polarisation is additive for the polar groups in a molecule containing more than one, provided that the solvation effects around each group are independent. Hence, in a two-group molecule it is $2\bar{\alpha}_s$, in a three-group one $3\bar{\alpha}_s$, and so on for still more complex ones.

The solvation polarisation in a molecule with one polar group only is negligible compared with the dipole orientation polarisation, but it may be important when the dipoles balance and the orientation polarisation is zero. Thus, for a molecule with two opposed dipoles of 2.5 D each, such as *p*-benzoquinone, this polarisation arising from one collinear and four zonal molecules around each group would be 4 c.c. considering

²¹ P. Debye, *Polare Molekeln*, Leipzig, 1929, p. 32.

only polarisation along the dipole axis; if we assume that the polarisability is roughly the same along the other two axes, the total polarisation is about 12 c.c. This is in as good agreement with the observed value^{22, 23} of 8.6-10 c.c. as the crudity of the treatment and the uncertainty about the values for some of the constants entitles us to expect. Two other non-polar diketones, tetramethyl-*cyclo*-butane-1, 3, -dione and carbon suboxide would be expected to have approximately the same polarisations as *p*-benzoquinone; the values are actually 11.0 and 10.4 c.c. respectively.

Comparison of the Jenkins-Bauer and Sutton-Frank Theories.

Magnitudes of Polarisation.—Jenkins used his equations only to calculate the relative magnitudes of the apparent orientation polarisations of related solutes in the same solvent, and did not attempt to calculate any absolute magnitude. It is, however, possible to do this.

Jenkins' formula for the polarisation of a compound with α balanced polar groups is

$$P = \frac{\alpha 4\pi N \mu_0^2}{2.9 \times k\alpha},$$

where N is the Avogadro number, k is the Boltzmann constant, and μ_0 is the average, observed moment in solution of a polar group. α is not the polarisability in Jenkins' notation but, as Bauer¹⁷ showed,

$$\alpha = \frac{b}{k} \left(\frac{\mu_0}{f\mu_g} \right)^2;$$

f occurs in the Higasi relation

$$\mu_0 = \mu_g(1 + fn),$$

where μ_g is the moment of the polar group determined in the vapour phase, and n is the number of solvent molecules per cubic centimetre. b is a factor in the expression for the probability of a fluctuation of n_0 to n , viz.,

$$dW = B_0 e^{-b(n-n_0)^2/kT} dn.$$

So it follows that

$$P = \frac{\alpha 2\pi N f^2 \mu_g^2}{9b}.$$

Now, Higasi showed that $f = 4\pi\alpha A$, where α is now the polarisability of a solvent molecule, and A is a geometrical factor depending only upon the shape of the solute molecule. The equation used by Bauer (see Tolman²⁴) is that

$$dW = B_0 e^{-(F-F_0)/kT} dx,$$

wherein F and F_0 are the free energies of the actual and average states, and x is some property such that $F - F_0$ can be expressed as

$$F - F_0 = b'(x - x_0)^2.$$

For a fluid,

$$F - F_0 = -\delta m \left(\frac{\partial p}{\partial v_0} \right) \frac{(v - v_0)^2}{2},$$

²² C. G. Le Fevre and R. J. W. Le Fevre, *J. Chem. Soc.*, 1935, 1696.

²³ D. L. Hammick, G. C. Hampson, and G. I. Jenkins, *Nature*, 1935, 136, 990.

²⁴ R. C. Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, New York, 1927, p. 320.

v and v_0 being specific volumes, and δm the mass of solvent considered, *i.e.*, the mass filling the sphere of influence of a solute polar group. For small fluctuations

$$(v - v_0)^2 = \frac{M^2}{N^2 d_0^2} (n - n_0)^2,$$

d_0 being the average density, M the molecular weight, and N Avogadro's number. Since

$$1/\beta = -v_0 \left(\frac{\partial p}{\partial v_0} \right) \text{ and } \delta m = \delta v d_0,$$

it follows that

$$F - F_0 = b(n - n_0)^2 = \frac{\delta v M^2}{2 N^2 \beta d_0^2} (n - n_0)^2.$$

Therefore

$$P = \frac{x 4 \pi N^3 f^2 \mu_g^2 \beta d_0^2}{9 \delta v M^2} = \frac{x 64 \pi^3 N^3 \alpha^2 A^2 \mu_g^2 \beta d_0^2}{9 \delta v M^2}.$$

For *p*-benzoquinone in benzene solution, *i.e.* with $x = 2$, $\alpha = 10^{-23}$ e.s.u., $A = -0.25$,* $\mu_g = 2.5$ D, $\beta = 6.6 \times 10^{-11}$, $d_0 = 0.87$, $\delta v = 10^{-21}$ c.c., $M = 78$, this gives $P = 0.003$ c.c. This is obtained on the basis of a sphere of influence equivalent to a cube of 10 Å edge: even if we take it as equivalent to one of only 4 Å edge P becomes only 0.047 c.c. It is improbable that the values taken for the constants can be very wrong, and it therefore appears that the fluctuation phenomenon does not explain the considerable value found for this compound.

The value of about 12 c.c. given by the Sutton-Frank expression for the same case is much nearer the observed one, 8.6-10 c.c. The value taken for the area of cross-section of a solvent molecule, 10 sq. Å may be rather small, for the effective area of a free molecule in a liquid is about 30 sq. Å, but it must be remembered that the molecule would not be entirely free, for its potential energy in the field of a dipole of the magnitude of that considered is comparable with the thermal energy at room temperatures.¹⁸ This last fact may mean also that the value taken for β is too high. Both of these possible errors would make the calculated value too large; but against this must be set the possible contributions of molecules in the second and more remote solvent layers. The direct influence of the original dipole falls off very rapidly, owing to the r^{-7} term, but the intermediate solvent molecules would relay its field and thus give it a larger effective sphere of influence. On the whole, therefore, it is probable that the calculated value is of the right order of magnitude.

One apparent difference in the conclusions from the two theories is that, unless we are to consider fluctuations within different parts of the sphere of influence, the Jenkins-Bauer effect can only occur when the polar group has its moment modified by the solvent, whereas the Sutton-Frank effect would occur whether it is modified or not, so long as there is solvent within the sphere of influence of the dipole.

Dependence upon Solute.—Both theories predict that the apparent orientation polarisation is proportional to μ_g^2 and to the number of polar groups in the molecule. The latter result is conditional upon the solvent effects for the several groups being independent, but owing to the small sphere of influence with which we are really concerned, this condition should frequently be satisfied. The apparent moments should

therefore be proportional to μ_0 and to the square root of the number of groups. As H. O. Jenkins remarked, these conclusions are in approximate agreement with the facts.

The Sutton-Frank effect should depend also upon the number of solvent molecules with which the solute dipoles might be in close contact, *i.e.*, upon the shape and extent of the dipolar groups.

Dependence upon Solvent.—The solvent dependent factor in the Jenkins-Bauer expression is $(\alpha^2 \beta d_0^2)/M^2$ which, by using the Clausius-Mosotti relation, can be transformed to $\beta(\epsilon - 1)^2/(\epsilon + 2)^2$. The factor in the Sutton-Frank expression is $\alpha^2 \beta(\epsilon + 2)^2/r^2 \epsilon^2$. r is really partly dependent upon the solute, but if we assume that, at least, $1/r^3$ and d_0/M are proportional, then by a similar transformation we find that the solvent factor is $\left(\frac{M}{d_0}\right)^{\frac{2}{3}} \left(\frac{\epsilon - 1}{\epsilon}\right)^2 \beta$. Approximate comparative values of these factors for some non-polar solvents are given below :—

Solvent.	Jenkins-Bauer factor.	Sutton-Frank factor.
<i>n</i> -Hexane	8.4	7.0
Carbon tetrachloride	9.6	7.5
Benzene	8.85	7.0
Carbon disulphide	11.8	9.3

According to either expression, therefore, there should be little variation of the polarisation with solvent except in the case of carbon disulphide. There are not many data which enable this conclusion to be tested, but those for *p*-benzoquinone show that the polarisation is the same in hexane, carbon tetrachloride, and benzene.^{22, 23}

Temperature Dependence.—Neither expression for polarisation is an explicit function of temperature. The Sutton-Frank expression would be if a full treatment were given, for since the polarisation arises from the combined effect of the dipole and applied fields in ordering the solvent molecules it would be reduced by an increase of thermal agitation. It can be seen, however, that this effect is not likely to be important, and that the neglect to take it into account is sufficiently justified, by recalling that the solvent molecules very close to the molecule, with which we are most concerned in this phenomenon, are not freely moving ones but are bound fairly tightly to it (Frank). Both expressions contain temperature-sensitive constants, the temperature-sensitive factors being βd_0^2 and $\beta(\epsilon + 2)^2/\epsilon^2 r^7$ respectively. For either benzene or carbon tetrachloride the temperature coefficients of β , d_0^2 , r^{-7} (assuming proportionality with $(d_0/M)^{7/3}$), and of $(\epsilon + 2)^2/\epsilon^2$ are about +0.008, -0.00245, -0.00285, and +0.0008 respectively. Thus, either expression should have a temperature coefficient of about +0.0055. Existing data^{22, 25} show no evidence of any positive coefficient, let alone of so large a one. It seems possible that the explanation of this, for the Sutton-Frank polarisation, is that the primary temperature effect mentioned above plays some part, and that the coefficient of compressibility really required, that of a solvent molecule under constraint, would not vary so rapidly with temperature.

Dependence upon Time Factors.—According to the Jenkins-Bauer theory the solute molecule becomes polar by differential solvation effects about the various polar groups in it and produces an extra polarisation by orienting in the applied field. This process requires a

²⁵ C. G. Le Fevre and R. J. W. Le Fevre, *J. Chem. Soc.*, 1935, 957.

definite time, of which the time of relaxation τ_R is a measure. It is obvious that for the acquired polarity to be fully effective it must be essentially constant over this time, *i.e.*, the period of fluctuation must be at least 10 times as great as τ_R . If the former is short in comparison, *i.e.*, $1/10$ of τ_R or less, there can be no orientation polarisation at all. If it is between these limits, the orientation is imperfect.

Now, observed relaxation times in benzene are of the order of 3×10^{-21} secs. (Debye²⁵). Periods of vibration of molecules against their neighbours, estimated in one of the customary ways (*cf.* Andrade²⁷) are of the order of 3×10^{-13} secs.: this is also the time required by a benzene molecule to move a distance of 1 Å, with the root mean square velocity given by kinetic theory, or for a sound wave in benzene to travel 3 Å. If instead we consider molecular vibrations governed by the force constant derived from compressibility, which was taken in the derivation of the expressions for polarisation to be the best basis for treating statistical density fluctuations, then we find a longer period for them, which is about equal to the relaxation time. The conclusion is that the ratio of times is probably such as to allow the Jenkins-Bauer effect to be partly but not completely operative, except in special cases.

The Sutton-Frank effect also depends upon the speed with which the solvent molecules can move, but in a different way. Except in very strong applied fields orientation is not involved, and hence the ratio of the time necessary for the new distribution of solvent molecules to be set up to the time of relaxation for orientation is immaterial. The ratio of the former time to the half-period of an alternating applied field must, however, be large. This condition is usually satisfied in dielectric constant measurements, but not in measurements of the refractive index for visible light: hence, this solvent effect could come into the measured total polarisation, but not the measured deformation polarisation. The degree of redistribution of solvent molecules does not depend upon their average speed *per se* but, as we have seen earlier, upon their average kinetic energy.

It is not suggested that the effect which we have described is the sole cause of abnormal moments of "non-polar" compounds, nor is it desired to place emphasis on the absolute value of it which has been calculated. We do consider, however, that it provides a possible explanation of some of the observed phenomena, and that it is free from some of the objections which apply to other attempts to explain them.

Summary.

A new, general solvent effect has been suggested and investigated theoretically. It arises from the combination of local dipole fields and the field applied for measurement in producing local changes of solvent density and thus of solvent effect upon apparent moment. Its value depends only upon the nature of the solvent, the moments of polar groups in the solute, and their number; it is independent of the total moment of the solute molecule. It is therefore not zero for non-polar molecules containing balanced polar groups, and may explain the anomalous apparent moments reported for a number of such substances.

²⁵ P. Debye, *Trans. Faraday Soc.*, 1934, **30**, 681.

²⁷ E. N. da C. Andrade, *Phil. Mag.*, 1934, **17**, 497, 698.

²⁸ (Sir) C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc., A*, 1927, **117**, 589.

²⁹ M. A. Govinda Rau, *Proc. Ind. Acad. Sci.*, 1934, **1**, 408.

The exact dependence of the effect upon solute, solvent, and temperature has been discussed. An absolute value for the polarisation of *p*-benzoquinone in benzene solution has been calculated, and is in good agreement with the observed value. The effect is compared with the one suggested by H. O. Jenkins and S. H. Bauer.

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ON MICRO THERMAL CONDUCTIVITY GAUGES.

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In following the progress of gas reactions in static systems manometric methods are often inapplicable. Gas analysis must therefore be employed to follow the course of the reaction, the whole sample being withdrawn from the reaction vessel at the termination of each run. This procedure unduly lengthens the completion of an investigation. Micro analytical methods on the other hand make it possible to follow the course of an individual run by the withdrawal of small samples from the reaction vessel at frequent intervals. In suitable cases a measurement of the thermal conductivity of the gas may suffice to yield the requisite information about its composition. Recently¹ some account has been given of the construction and application to the analysis of hydrogen-deuterium mixtures of a small volume (0.2 c.c.) thermal conductivity gauge. It seemed that such a gauge would have applications in a number of other directions; in this paper several modifications in design are described and an approximate theory worked out in order to demonstrate the wide applicability of this micro-method of gas analysis.

Experimental.

A number of improvements in the design of these gauges may be described first of all. By adopting the following method of construction the volume of the cell has been reduced to 0.05 c.c. 2 mm. capillary tubing is drawn down to an internal diameter of 0.7 mm. A uniform length is sealed to 2 mm. tubing at *aa* (Fig. 1). The platinum stirrup with attached 0.015 mm. platinum wire is inserted and the ring seal (*bb*) made in the usual manner. The lead to which the other end of the platinum filament is attached is sealed to the glass tube at *c* with a minute pointed flame. If necessary the filament may easily be made taut, by gently heating the end of the tube and pulling the lead cautiously. This operation is best followed by means of a low-powered microscope. The cell is then mounted on the compression capillary of a McLeod gauge.²

As will become evident in what follows it is an advantage in certain analyses to have a thick filament in the gauge. It is, however, difficult

¹ Melville and Bolland, *Proc. Roy. Soc., A*, 1937, 160, 384.

² Reference ¹, Fig. 1.

to measure the resistance of such a filament with the accuracy and reproducibility here required, since lead and contact resistances are comparable with that of the filament. This disability can easily be removed by using a spiral tungsten filament of close pitch similar to those employed in gas-filled incandescent lamps. This combines the advantages of both high resistance and thick filament gauges. The coiled filament gauge is constructed in a similar manner to the straight wire model, except that the internal diameter must be increased (to, say, 2 mm.) to accommodate the spiral. In one typical gauge, carrying a filament of wire radius 0.05 mm., spiral radius 0.7 mm., length 20 mm. and resistance at 20° C. of about 14 ohms, the volume of gas required for an analysis was 0.005 c.c. at N.T.P.—a three-fold diminution on the figure for the straight-filament gauge. Operating the gauge as before,¹ the resistance values obtainable were sufficiently stable to allow for measurement to 0.001 ohm. In one instance corresponding resistance values for hydrogen and deuterium were found to be 19.643 and 21.462 ohms respectively. As the variation in resistance value amounted to 0.0013 ohms per 0.1 mm. Hg (the estimated error in gas-pressure measurements) the experimental error in the measured deuterium contents of hydrogen-deuterium mixtures would appear to be not greater than 0.1 per cent. This represents a fourfold improvement on the accuracy of the earlier gauges.

For the estimation of *para*-hydrogen the gauge must, of course, be cooled in liquid air. This is simply accomplished as shown in Fig. 2. The capillary connecting the gauge to the compression capillary of the

McLeod bulb is 0.5 mm. bore and therefore of small volume compared with the gauge. With a compression capillary of internal diameter 2 mm. and length 20 cm., the volume of the sample to be analysed may range from 0.010 to 0.030 c.c. at N.T.P., the pressure at which the conductivity is measured being 50 mm. For some purposes, no less than 3 watts were dissipated in the gauge filament, thus causing accelerated evaporation of the surrounding liquid air. The temperature of the bath accordingly rises owing to partial fractionation of the liquid air, thus necessitating frequent standardisations of the gauge. Consequently it is advantageous to use liquid oxygen or liquid nitrogen to avoid this complication.

As is customary, the gauge was inserted in a Wheatstone bridge. Provision was made for two alternative methods of operation: a constant voltage could be applied across the bridge and the equilibrium resistance of the wire measured by means of a four-dial resistance box; alternatively, a variable voltage could be applied across the bridge, so that the resistance

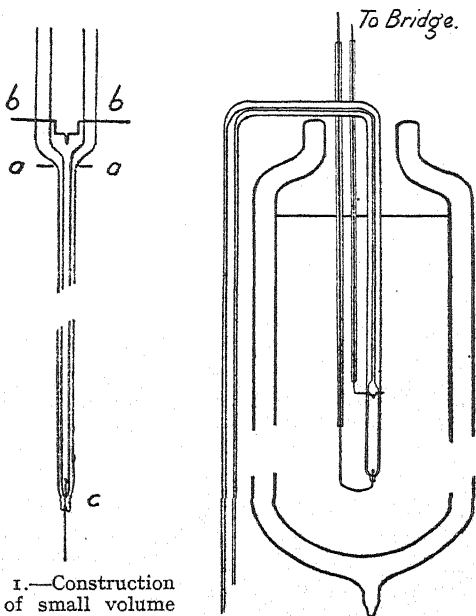


FIG. 1.—Construction of small volume thermal conductivity cell.

FIG. 2.

of the wire could be maintained at a constant value. This voltage was measured by a potentiometer reading to 0.0001 volts. The accuracy of both methods was approximately equal, though the variable voltage method appeared somewhat more tedious to operate in practice.

End Corrections.

Before developing the theory of the straight-wire gauge, it is necessary to estimate the magnitude of the end corrections. Following Gregory and Archer³ the heat (E) flowing from the filament to each lead when the steady state has been attained is given by

$$E = \frac{Q \cdot K \cdot A}{\sqrt{P}} (1 - e^{-\sqrt{P} \cdot 2l}), \quad (1)$$

where A and $2l$ are the area of cross-section and length of the wire respectively. P and Q are defined by the equations

$$P = \frac{2\pi K_g}{K_M A \ln r_2/r_1} - \frac{i^2 \rho_0 \alpha}{J \cdot K_M A^2}, \quad Q = \frac{i^2 \rho_0}{J \cdot K_M A^2}$$

where K_g is the thermal conductivity of the gas and K_M that of the wire; r_1 and r_2 are the radii of wire and tube respectively; ρ_0 refers to the specific resistance of the wire at 0° C. and α to the temperature coefficient of ρ_0 . The following were the dimensions of a typical gauge wire: $2l = 7.30$ cm., $r_1 = 0.00075$ cm., $r_2 = 0.100$ cm., $i = 0.154$ amps. For a platinum wire $\rho_0 = 10^{-5}$ ohms, $\alpha = 3.7 \times 10^{-3}$ ohms/°C and $K_M = 0.155$ cal./cm.²/sec./°C. K_g is the conductivity of hydrogen at 50 mm. This was calculated from measurements of the conductivity at 50 mm. relative to that at infinite pressure and amounted to 2.30×10^{-4} cal./cm.²/sec./°C. Substituting in (1) the total end losses were calculated to be 1.87×10^{-3} cal./sec., corresponding to 0.6 per cent. of the total electrical input. For the present, then, the end losses may be neglected.

Theory of the Gauge.

Calculations on the theory of the "constant-voltage" method of operating the gauge are considerably simplified by changing the "resistance values" into the voltages required to balance the bridge with the gauge filament at a definite resistance. At high pressures, the electric energy supplied to the filament is almost wholly conducted away by the gas. Then

$$(q =) \frac{V^2}{R} = \text{const.} (T_1 - T_0) \cdot K,$$

where V is the voltage across the filament, of resistance R , and at temperature T_1 ; T_0 is the temperature of the gauge wall and K the thermal conductivity of the gas at the mean temperature, $\frac{T_1 + T_0}{2}$.

From data given in International Critical Tables, the following relation was deduced (for the particular filament)

$$T_1 - T_0 = 0.797 (R_1 - R_0) \quad (2)$$

where R_1 and R_0 are the resistances of the filament at temperatures T_1 and T_0 .

³ *Proc. Roy. Soc., A*, 1926, 111, 95.

Since the thermal conductivities of gases are markedly dependent on temperature, it is necessary to take this factor into account. Gregory finds the thermal conductivity of hydrogen in the temperature range 270 — 500° K. expressible by

$$K_{H_2} = 5.68 \times 10^{-6} \times T^{0.77}$$

Employing this relation,

$$\frac{K'}{K} = \left(\frac{T_1 + T_0}{2T_0} \right)^{0.77}$$

= const. $(R_1 + R_0)^{0.77}$, by application of (2). K represents the conductivity of hydrogen at temperature, T_0 .

Since the voltage, V_A , applied to the bridge is distributed over the filament (resistance, R_W), the leads (R_L) and the series resistance (R_S) in the adjacent arm of the bridge,

$$V = \frac{V_A \cdot R_W}{R_W + R_L + R_S}$$

If then, R_{H_2} and R_M represent the observed resistance values for hydrogen and say a hydrogen-deuterium mixture, respectively, when a voltage V_A is applied to the bridge,

$$\left(\frac{K_{H_2}}{K_M} \right)_{T_0} = \frac{R_{H_2}}{R_M} \cdot \left(\frac{R_M + R_L + R_S}{R_{H_2} + R_L + R_S} \right)^2 \cdot \frac{R_M - R_0}{R_{H_2} - R_0} \cdot \left(\frac{R_M + R_0}{R_{H_2} + R_0} \right)^{0.77} \quad (3)$$

In a typical gauge $R_0 = 45.40$, $R_L = 0.90$, $R_S = 10.00$, $R_{H_2} = 62.10$ and $R_{D_2} = 64.90$ ohms. Substituting in (3) $K_{H_2}/K_{D_2} = 1.235$. Theoretically this ratio should be 1.414, which value has been confirmed experimentally by Van Cleave and Maass,¹⁰ and by Northduft.¹³ The discrepancy between these observed and theoretical values is sufficiently marked to necessitate some explanation.

When the diameter of the filament of a conductivity gauge is of the order of 0.01 mm., the observed conductivity of a gas is not independent of pressure, even at pressures as high as 50 mm.: there is an appreciable temperature discontinuity at the gas solid interface. The quantitative theory of the magnitude of this discontinuity has been developed by Gregory^{3, 4} following Smoluchowski's treatment.⁵ The final relationship between the heat (q), conducted from unit length of a fine wire axially disposed in a cylindrical tube, and pressure may be expressed in the form:

$$T_1 - T_0/q = \frac{\ln . r_2/r_1}{2\pi K} + \sqrt{T_1} \cdot S \cdot \frac{1}{p} - \frac{q \cdot S^2}{(2 - \alpha)} \cdot \frac{1}{p^2} \quad (4)$$

where T_1 and T_0 are the temperatures of the wire and the wall respectively, r_1 and r_2 the radii of cross-section of the wire and tube, K is the mean thermal conductivity of the gas and S is given by

$$S = \frac{1}{r_1} \cdot \sqrt{\frac{M}{2\pi R}} \cdot \frac{1}{(C_v/R + \frac{1}{2})} \cdot \frac{2 - \alpha}{2\alpha},$$

where M is the molecular weight of the gas, and α the accommodation coefficient of the gas on the wire. It is evident that this expression reduces to the general form:

$$\frac{1}{V^2} = A + \frac{B}{p} - \frac{CV^2}{p^2}, \quad (5)$$

⁴ *Phil. Mag.*, vii, 1936, 22, 257.

⁵ *Ann. Physik*, 1911, 35, 983.

where V is the voltage applied to the gauge to maintain the filament at a definite temperature, and A , B and C are constants for a given gauge, gas and filament temperature. Farther, for the same gauge and filament temperature, these constants may be calculated for any gas, from their values for one particular gas (here, hydrogen) and the value of the accommodation coefficient relative to that of the standard gas under the same conditions.

Thus

$$\left. \begin{aligned} A &= \frac{K_{H_2}}{K} \cdot A_{H_2} = \sqrt{\frac{M}{M_{H_2}}} \cdot A_{H_2} \\ B &= \sqrt{\frac{M}{M_{H_2}}} \cdot \frac{2 - \alpha}{2 - \alpha_{H_2}} \cdot \frac{\alpha_{H_2}}{\alpha} \cdot B_{H_2} \\ C &= \left(\frac{B}{B_{H_2}} \right)^2 \frac{2 - \alpha_{H_2}}{2 - \alpha} \end{aligned} \right\} \quad (6)$$

where the symbols with the suffix, H_2 , refer to hydrogen and those without suffixes to the second gas. In view of the occurrence of the factor $(2 - \alpha)$ in the above equations it was necessary to evaluate absolutely the accommodation coefficient of hydrogen, from measurements of the thermal conductivity of hydrogen at low pressures (ca. 0.05 mm.) in conjunction with the relation :

$$q = 2\pi r_1(T_1 - T_0)C_v \cdot \frac{p}{(2\pi mkT_0)^{\frac{1}{2}}} \cdot \alpha$$

The value obtained—0.29—is in agreement with previous determinations, under similar conditions.

The values of A , B and C for hydrogen were determined from an extensive series of conductivity measurements over a wide range of pressure. Since at high pressures (above 200 mm. in this case) the term $C/p^2 \cdot V^2$, in equation (5), is of but negligible importance, a linear relationship exists between $1/p$ and $1/V^2$, the slope and intercept on the $1/V^2$ -axis of which determine B and A respectively. C may be calculated from the following relation, obtained by comparison of (4) with (5) :

$$C = B^2 \cdot \frac{T_1 - T_0}{T_1(2 - \alpha)} \quad (7)$$

Using this value of C , the values of V^2 corresponding to lower values of pressure were calculated and compared with experimental data. Table I. which gives a few such comparable figures, serves to show the validity of the equation

$$\frac{1}{V_{H_2}^2} = 0.00588 + \frac{0.254}{p} - \frac{0.0131}{p^2} \cdot V_{H_2}^2 \quad (8)$$

at pressures in excess of 15 mm.

Measurement of the accommodation coefficient of deuterium relative to that of hydrogen gave $\alpha_{D_2}/\alpha_{H_2} = 1.30$, in agreement with Mann and Newell's determination.⁶ Employing equations of the type of (6) the dependence of the conductivity of deuterium (αV^2) on pressure was calculated as

$$\frac{1}{V_{D_2}^2} = 0.00831 + \frac{0.265}{p} - \frac{0.0148}{p^2} \cdot V_{D_2}^2 \quad (9)$$

⁶ *Nature*, 1936, 137, 662.

Equations (8) and (9) would indicate that at pressures of 50 mm., the apparent conductivities of hydrogen and deuterium are in the ratio 1.24 : 1.00. The agreement with the experimentally determined value (1.235 : 1.00) will be noted.

A second feature of the analyser readings which is not in accord with simple kinetic theory considerations is the form of the calibration curves for H_2 - D_2 mixtures and also similar mixtures in which the equilibrium $H_2 + D_2 \rightleftharpoons 2HD$ is established.⁷ Fig. 3 indicates the dependence of the thermal conductivity of such mixtures on composition, calculated from these curves by the method indicated on p. 2, while Fig. 4 shows the form of similar curves deduced from the simple theory that the conductivity of a mixture is given by

$$K_M = f_1 K_1 + f_2 K_2 + f_3 K_3 \dots$$

where f_n and K_n refer to the partial pressure and thermal conductivity of the n th component. In this case $K_{H_2} : K_{HD} : K_{D_2} =$

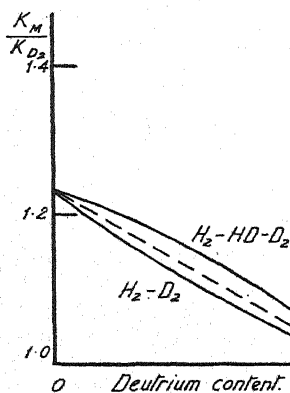


FIG. 3.

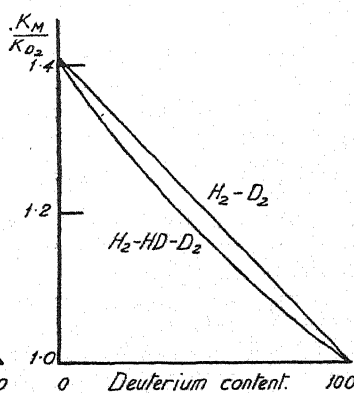
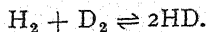


FIG. 4.

The relative conductivity of H_2 - D_2 and equilibrium H_2 - HD - D_2 mixtures as obtained experimentally (Fig. 3) and from simple kinetic theory (Fig. 4).

1 : 1.5⁻¹ : 2⁻¹, while f_{H_2} , f_{HD} and f_{D_2} may readily be calculated from the constant of the equilibrium



At the temperature of the nickel wire, used to prepare the equilibrium mixtures for calibration purposes, the constant has the classical

⁷ Melville and Bolland, *loc. cit.* ¹, Fig. 3.

value of four. In addition, then, to the difference in the relative magnitude of K_{H_2} and K_{D_2} in the two cases, the two sets of curves are quite differently disposed with respect to the line drawn between K_{H_2} and K_{D_2} .

The temperature-drop effect furnishes an explanation of most—but not all—of the discrepancy. In order to obtain an equation expressing the conductivity of HD in the manner of (5), it was necessary to determine the relative value of the accommodation coefficient of HD. This was obtained from low-pressure conductivity measurements of 1:1 hydrogen-deuterium mixtures before and after establishment of the $H_2 + D_2 \rightleftharpoons 2HD$ equilibrium. The relative accommodation coefficient of HD was determined from the relation

$$\frac{S_{H_2-HD-D_2}}{S_{H_2-D_2}} = \frac{f_{H_2}^{eq} + f_{HD}^{eq} \frac{\alpha_{HD}}{\alpha_{H_2}} + f_{D_2}^{eq} \frac{\alpha_{D_2}}{\alpha_{H_2}}}{f_{H_2} + f_{D_2} \cdot \frac{\alpha_{D_2}}{\alpha_{H_2}}} \quad (10)$$

where S refers to the slopes of the linear $(V^2 - V_0^2)/p$ curves, as determined for example from the typical data given in Table II.

TABLE II.

Gas.	D-Content (Per Cent).	p (mm. Hg).	$V^2 - V_0^2$.	$\frac{S_{H_2-HD-D_2}}{S_{H_2-D_2}}$.
H_2-D_2	51	0.1060	1.712	1.050
H_2-HD-D_2	—	0.1060	1.800	
H_2-D_2	50	0.0701	1.371	1.048
H_2-HD-D_2	—	0.0689	1.415	

f^{eq} and f refer to the partial pressures of the several components of equilibrium mixtures of H_2 , HD and D_2 , and of H_2-D_2 mixtures respectively. For an equilibrium mixture of D-content 50 per cent., $f_{H_2}^{eq}$, f_{HD}^{eq} and $f_{D_2}^{eq}$ may be taken as 0.25, 0.50 and 0.25 respectively. Taking $S_{H_2-HD-D_2}/S_{H_2-D_2} = 1.049$ (Table II.), and $\frac{\alpha_{D_2}}{\alpha_{H_2}} = 1.30$ (p. 1320), equation (10) yields the value of 1.30 also for α_{HD} . The explanation of this abnormally large value of α_{HD} may lie in the fact that the rotational accommodation coefficient of the HD molecule is higher than some mean value between α_{H_2} and α_{D_2} owing to the successive rotational energy levels becoming more easily excited than the alternate rotational levels of symmetrical molecules existing in *ortho*- and *para*-modifications.

From the appropriate equations of type (6), the pressure-conductivity relation for HD may be obtained as

$$\frac{1}{V_{HD}^2} = 0.00720 + \frac{0.228}{p} - \frac{0.0111}{p^2} V_{HD}^2 \quad (11)$$

From (8), (11) and (9), then, the apparent conductivities of H_2 , HD and D_2 at 50 mm. are in the ratio 1.24:1.15:1.00. Assuming that these conductivities are additive a curve may be constructed from the equation

$$(K_M)_{50 \text{ mm.}} = f_{H_2}(K_{H_2})_{50 \text{ mm.}} + f_{HD}(K_{HD})_{50 \text{ mm.}} + f_{D_2}(K_{D_2})_{50 \text{ mm.}}$$

The calibration curve obtained in this way is close to, but not coincident with, the experimental curve as may be seen from Table III., in which

the observed and computed relative conductivities of equilibrium H_2 -HD- D_2 mixtures, of various deuterium-contents, are presented.

Similar considerations would indicate a perfectly linear curve for H_2 - D_2 mixtures, while that actually obtained departs slightly from linearity. The magnitude of the divergence is indicated in Table III.

It is a well-known fact that, even under conditions where no interfacial temperature

drop effect is in operation, the conductivity of a mixture is not expressible by a relation of the simple form

$$K = f_1 K_1 + f_2 K_2 \dots \dots \dots (12)$$

where K is the thermal conductivity of a mixture containing components whose partial pressures are $f_1, f_2 \dots$ and thermal conductivities $K_1, K_2 \dots$ respectively. Some attempts, *e.g.*,^{8,9} have been made to give a theoretical explanation of such observed divergences, but without achieving any real success. Thus by taking into account the mutual effect of the various components on the mean free path of their molecules a relation may be obtained which indicates deviations from (12) which though in the right direction are in most cases much too small in magnitude.⁹ In view of the equality of the mean free paths of the three components here concerned this complication would in any case not arise here. It may be noted that Van Cleave¹⁰ has found a mixture effect in the case of H_2 - D_2 in the same direction and of the same magnitude as that found above: from his results the ratio of the "linear" to the observed conductivity for a mixture of deuterium content of 50 per cent. is 1.00 compared with 1.015 above.

Analysis of Ortho-Para-Hydrogen Mixtures.

By adapting the gauge for operation at temperatures in the range in which the difference in the rotational specific heats of the *ortho*- and *para*-modifications of hydrogen is significant, a reliable and convenient method of analysing *ortho-para* hydrogen mixtures has been made available.

For this particular purpose a spiral gauge of the type indicated in Fig. 2 was employed. No special precautions as to the maintenance of constant level in the surrounding liquid oxygen bath were found necessary: provided the cell and the bi-metallic lead junctions were completely immersed, variation of the gauge readings under standard conditions was quite inappreciable in the course of a day, and indeed from day to day. As before, measurements were made at a gas pressure of 50 mm.

For the purpose of determining optimum conditions for the operation

⁸ Weber, *Ann. Physik*, 1917, 45, 481.

⁹ Schmick, *Physikal. Z.*, 1928, 29, 633.

¹⁰ Van Cleave, *Can. J. Research*, B, 1935, 13, 384.

TABLE III

D-Content.	$\text{H}_2 - \text{HD} - \text{D}_2$.		$\text{H}_2 - \text{D}_2$.	
	Relative Conductivity.		Relative Conductivity.	
	Obs.	Calc.	Obs.	Calc.
0	1.235	1.235	1.235	1.235
10	1.220	1.216	1.204	1.212
30	1.186	1.177	1.152	1.165
50	1.145	1.135	1.101	1.117
70	1.096	1.085	1.056	1.070
90	1.034	1.029	1.015	1.023
100	1.000	1.000	1.000	1.000

of the gauge, some measurements were made with hydrogen samples containing 25 per cent. and 70 per cent. *para*-hydrogen. The latter was prepared by adsorbing purified hydrogen on a well-outgassed sample of activated charcoal, maintained at a temperature of 56° K. by immersion in a liquid oxygen bath, the pressure above which was reduced to 5 mm. by evacuation.

From gauge readings for these two samples, using the variable voltage method, with the filament at various temperatures, the optimum sensitivity of the gauge for this particular type of analysis appears to correspond to filament temperatures of about 200° K., though as is evident from Table IV., there is no sharply defined optimum temperature.

TABLE IV.

$T_{\text{wire}} (^{\circ}\text{K.})$	107	145	183	277	391
$\frac{V_{25}^2}{V_{25}^2} (50 \text{ mm.})$	1.052	1.078	1.084	1.059	1.025

In order to account quantitatively for these values the dependence of conductivity on pressure at the filament temperatures in question was investigated. At pressures above 200 mm. reasonably linear $1/V^2 - 1/p$ graphs were obtained, but below such pressures very considerable deviations set in. Table V. gives the constants in the general equation

$$1/V^2 = B + C/p$$

obtained under the various temperature conditions from high pressure measurements.

TABLE V.

p -Content (Per Cent.) of Hydrogen.	Wire Temp.	B.	C.	$(1/V^2)_{50}$.
25	107	1.301	3.02	1.349
70	—	1.205	3.42	1.281
25	145	0.2732	0.94	0.2828
70	—	0.2486	1.02	0.2622
25	183	0.1126	0.470	0.1192
70	—	0.1020	0.520	0.1100
25	277	0.02787	0.223	0.3150
70	—	0.02629	0.246	0.02974
25	391	0.01015	0.124	0.01217
70	—	0.00977	0.126	0.1187

The values of $1/V^2$ at pressures of 50 mm. are also included, in order to demonstrate the relatively small effect of reducing the pressure from infinity ($B = 1/V^2$, at infinite pressure).

The relative conductivities of the two mixtures under the requisite temperature conditions have been calculated and found to be in satisfactory accord with the experimental data. The thermal conductivity of a gas may be expressed in the well-known form

$$K = f \cdot \eta \cdot C_v \quad (13)$$

where η and C_v represent the viscosity and specific heat at constant volume of unit mass of the gas. The factor f is itself a function of C_v . For diatomic gases, Jeans derives the relation

$$f = \frac{1}{4}(9\gamma - 5) \\ = \frac{1}{2}(2C_v + 9)/C_v \quad (14)$$

where γ is the ratio of the specific heats at constant pressure and volume.

The data given by Giaque,¹¹ as amended by Davis and Johnston,¹² have been used to give values of C_v in the required temperature range. By calculating K from (13) at regular temperature intervals—making due allowance for the variation of η with temperature by means of the equation $\eta = \eta_0 \left(\frac{T}{273} \right)^{0.695}$, where η_0 is the viscosity of hydrogen at 273° K.—curves representing the variation of the conductivity of pure *ortho*- and *para*-hydrogen with temperature were constructed. Similar curves for *o-p* mixtures containing 25 and 70 per cent. *p*-hydrogen were then obtainable, on the assumption that mixture effects were absent.

Integration between the appropriate temperature limits, by means of a large-scale K-T graph and planimeter, enabled the theoretical relative conductivities to be calculated for the various wire temperatures, in accordance with

$$q = \text{const.} \int_{T_1}^{T_2} K \cdot dt,$$

where q represents the heat conducted from the wire, and T_1 and T_2 are the temperatures of the wire and wall.

That the conductivity ratios obtained in this way compare favourably with the observed values—obtained by extrapolation of $1/V^2 - 1/p$ curves to infinite pressure—is shown in Table VI.

TABLE VI.

Temp. of Wire (°K.).	K_{75}/K_{25} (Calc.).	V_{75}^2/V_{25}^2 .
107	1.080	1.079
145	1.104	1.099
183	1.100	1.104
277	1.057	1.059
391	1.030	1.025

Experimental Method of Analysis.

As before, the most convenient method of operating the gauge would seem to be the "constant voltage-variable resistance" method. Preliminary measurements will serve to give some indication of the accuracy of analysis to be expected. Thus, for example, with a definite voltage across the bridge of about 4, the equilibrium temperatures attained by the filament of a typical spiral gauge, when surrounded in turn by hydrogen samples (at 50 mm. pressure) of para-contents of 70 per cent. and 25 per cent. corresponded to resistance values of 8.109 and 8.582 ohms, respectively. The resistance of the filament at 90° K. was 3.620 ohms; the respective equilibrium temperatures were 174° K. and 183° K. The experimental error (0.1 mm.) involved in the measurement of the pressure of the sample being analysed would cause an uncertainty of only 0.0003 ohms in the resistance values. Assuming that here also this represents the main source of inaccuracy, it should be possible to estimate the *para*-content of hydrogen samples to ± 0.2 per cent.

Analysis of Ternary Mixtures.

Micro-methods for the analysis of hydrogen and deuterium in gas mixtures depend on freeing these components from the other gases. This is easily accomplished with liquid air boiling at reduced pressure, except when the following gases are present: N_2 , O_2 , CO , CH_4 and the inert gases. These can only be thoroughly removed by means of liquid hydrogen—a refrigerant which is not always available for use. The following method,

¹¹ J. Amer. Chem. Soc., 1930, **52**, 4816.

¹² Ann. Physik, 1937, **28**, 157.

¹² Ibid., 1934, **56**, 1045.

however, enables the analysis of mixtures of hydrogen, deuterium and one non-condensable gas to be carried out without the use of liquid hydrogen.

The method depends on the non-classical variation of the rotational specific heat of hydrogen with temperature. From the data, given by Giauque¹¹ and Johnston and Long,¹² for the rotational specific heat of hydrogen and deuterium, the relative thermal conductivities for the two isotopes have been calculated, at various temperatures. Combining equations (13) and (14)

$$K_{H_2}/K_{D_2} = \frac{2(C_v)_{H_2} + 9}{2(C_v)_{D_2} + 9} \times 1.414.$$

This involves the assumption that the temperature coefficient of viscosity is the same for H_2 and D_2 .

TABLE VII.

T (° K.)	50	100	150	200	250	300
K_{H_2}/K_{D_2}	1.120	1.147	1.272	1.344	1.384	1.403

Evidently, then, the relative conductivities of H_2 and D_2 may be very appreciably altered by working at low (*ca.* 100° K.) and high (>300° K.) temperatures. In general, the specific heat of the non-condensable gas will be constant down to at least liquid oxygen temperatures; the conductivity relative to that of deuterium, will vary but little, the actual magnitude depending on the Sutherland constant of the particular gas. Hence, by operating the gauge at two-wire temperatures (about 110° K. and 300° K.) with the wall temperature at 90° K., conductivity diagrams of the type indicated in Figs. 5A and 5B might be expected. At the low

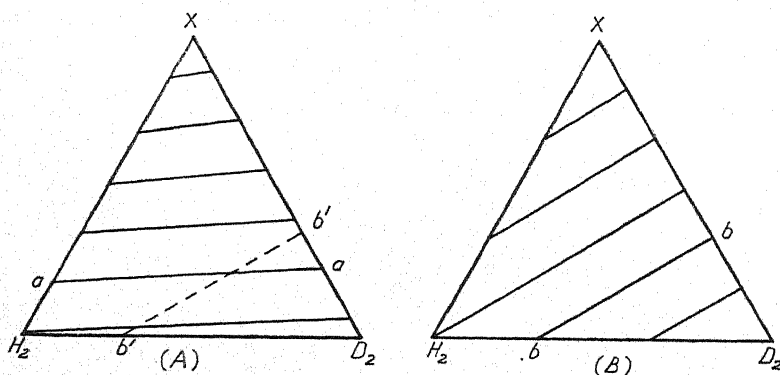


FIG. 5.—Calibration curves for analysis of ternary mixtures :

(A) for low filament temperatures (*ca.* 110° K.).

(B) for high filament temperatures (*ca.* 300° K.).

temperature, the tie-lines indicating the ternary mixtures of different composition having the same apparent conductivity, are almost parallel to the H_2 — D_2 side of the triangle, while at the higher wire temperature they make a quite definite angle with it. Suppose an unknown mixture is passed into the cell and the apparent conductivity (measured by the "constant resistance-variable voltage" method) is found to correspond to the lines *aa* and *bb* at the low and high wire temperatures respectively, then the composition of the mixture is given by the intersection of *aa* and *bb* (as shown by the dotted line in Fig. 5A).

Method of Calibration.

It is convenient for calibration purposes to have reservoirs of the three separate gases attached to the apparatus, through capillary pipettes. The voltage values, for the two-wire temperatures, for the several gases are determined first; next, the gauge is calibrated for three series of binary mixtures, and finally a few calibrations for ternary mixtures, in order to determine any curvature of the iso-volt lines, may be carried out. The mixtures are made up at low pressures with the help of an ordinary Pirani gauge, calibrated for the three gases. For the success of this method of analysis it is, of course, essential that the gauge should give reproducible readings over long periods of time. The spiral gauges have been found eminently satisfactory in this respect, presumably since here the accommodation coefficient effect is practically negligible.

In the absence of mixture effects, the conductivity of a mixture (αV_M^2) should be given by

$$V_M^2 \alpha (f_{H_2} K_{H_2} + f_{D_2} K_{D_2} + f_N K_N),$$

where f and K refer to the mole-fractions and conductivities of the three components, with the result that linear "iso-voltage" lines should be obtained. Actually, in a calibration of the gauge for analysis of H_2 - D_2 - N_2 mixtures it was found that this simplification was not obtained, the iso-volt lines at the higher wire temperature showing definite curvature. These particular calibration curves are reproduced in Fig. 6. Here, triangular paper has been dispensed with by plotting on squared paper the mole-fraction of nitrogen as ordinates and the mole-fraction of deuterium in the hydrogen gas as abscissæ. The tie-lines refer to definite values of V_M/V_{N_2} . (It is, of course, unnecessary to work with the more theoretically-significant V^2 values.)

It will be seen that the low and high temperature iso-volt lines cut at a sufficiently large angle to permit of the composition being estimated to about 1 per cent., if the nitrogen content is not large. Naturally at high nitrogen contents, the estimation of the D-content is not quite so accurate.

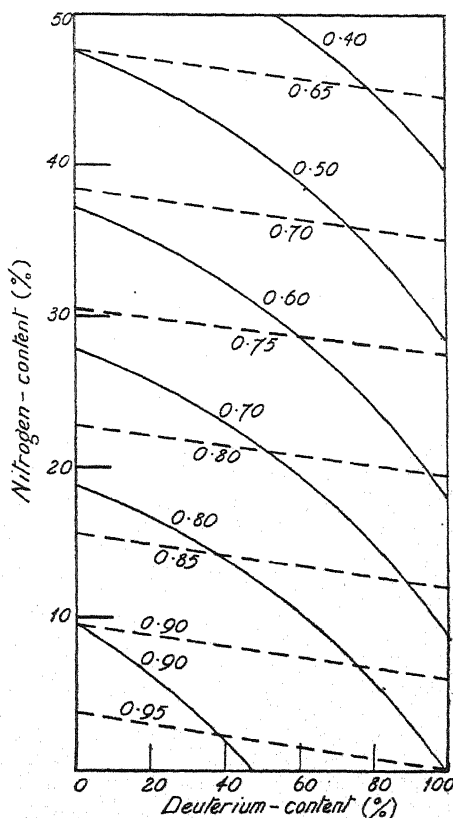


FIG. 6.—Calibration curves for analysis of H_2 - D_2 - N_2 mixtures:

full lines: high filament temperature ($340^\circ K.$)
broken lines: low filament temperature ($115^\circ K.$)

The value of V_M/V_{N_2} corresponding to each iso-voltage line is indicated.

In order that the choice of operating conditions may readily be made, the following Table summarises the most suitable gauge for any specific purpose. It will be seen that the spiral wire gauges have the widest applicability. Incidentally they are the most convenient to use as the pressure adjustment is not so critical as that with the straight wire gauges. If liquid air is not available and HD analyses are required, then the straight wire type must be employed.

Purpose.	Type of Gauge and Operating Conditions.		
		Wire Temp. °K.	Bath Temp. °K.
D-content of hydrogen gas, not sensitive to HD molecules . . .	Spiral	350	293
D-content of hydrogen gas, sensitive to HD molecules . . .	Straight *	350	293
Sensitive to HD, insensitive to D ₂ molecules . . .	Spiral	180	90
Estimation of <i>para</i> hydrogen (or <i>ortho</i> deuterium) . . .	Spiral	115	90
Analysis of ternary mixtures . . .	Spiral	180	90
		115	
		340	90

* 0.015 mm. diameter wire.

The spiral gauge dipping into liquid air has also the following advantage. If the hydrogen-deuterium ratio is required in a mixture when the gases C₂H₂, C₂H₄, C₂H₆, CO₂, N₂O, PH₃, SbH₃ or SiH₄ are present, it is necessary to employ a pumped-out liquid air trap with a gauge operated at a bath temperature of 20° C. to free the hydrogen gas from these molecules. But with a gauge cooled in liquid air, these gases have a negligible vapour pressure compared with 50 mm., the standard pressure of hydrogen gas used in the gauge, and do not therefore interfere with the analysis.

Summary.

Improvements in the design of a small volume thermal conductivity cells, suitable for the microanalysis of gas mixtures are described. The volume of the cells may be reduced to 0.05 c.c., thus permitting the analysis of 0.005 c.c. (at N.T.P.) of binary mixtures, the constituents of which possess different thermal conductivities.

A theory has been developed to account for the behaviour of the gauges when filled with hydrogen, deuterium, H₂—D₂, and H₂—HD—D₂ mixtures. As a result conditions have been defined so that a gauge will or will not discriminate between equilibrated and non-equilibrated hydrogen-deuterium mixtures.

The optimum conditions for the analysis of *ortho-para* hydrogen mixtures has also been worked out.

By making use of the variation of rotational specific heats of hydrogen and deuterium with temperature, a method is described for the analysis of ternary mixtures containing hydrogen, deuterium and a third constituent, non-condensable in liquid air, such as CO, CH₄, O₂, N₂ and the inert gases. The method is also applicable to any ternary mixture having hydrogen as one constituent provided that the thermal conductivities of the other two constituents are different.

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THE ESTIMATION OF HYDROGEN DEUTERIDE BY MEANS OF THE MICRO THERMAL CONDUCTIVITY GAUGE.

BY G. H. TWIGG.

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The measurement of hydrogen deuteride (HD) in mixtures of hydrogen and deuterium is carried out by means of the micro thermal conductivity gauge of Melville.¹ It has been pointed out in the foregoing paper that, with gauges employing a fine wire and used at room temperature, there is a difference in the effective thermal conductivity of a mixture of hydrogen and deuterium and that of the same mixture when it has been brought to equilibrium. By taking advantage of this difference it has been found possible to measure the fraction of hydrogen deuteride in mixtures not completely at equilibrium.

Any mixture of H_2 , HD and D_2 of total deuterium content u can be regarded as made up of two parts:—a fraction x at equilibrium and the other fraction $(1-x)$ composed of H_2 and D_2 only, each fraction having a deuterium content u . If the mixture has the composition $aH_2 + bHD + cD_2$, where a , b , and c are the respective mole fractions of the three species, then

$$\begin{aligned} a + b + c &= 1 \\ c + b/2 &= u. \end{aligned}$$

In the fraction $(1-x)$ of non-equilibrium hydrogen of deuterium content u

$$\begin{aligned} [H_2] &= (1-x)(1-u) \\ [D_2] &= (1-x)u. \end{aligned}$$

Hence, in the fraction x of equilibrium hydrogen

$$\begin{aligned} [H_2] &= a - (1-x)(1-u) = 1 - b/2 \\ &\quad - u - (1-x)(1-u) = x(1-u) - b/2 \\ [HD] &= b \\ [D_2] &= c - (1-x)u = u - b/2 - (1-x)u = xu - b/2. \end{aligned}$$

But for this fraction $\frac{[HD]^2}{[H_2][D_2]} = 4$. On substitution this yields

$$b = 2xu(1-u), \quad \dots \quad (1)$$

¹ Melville and Bolland, *Proc. Roy. Soc., A*, 1937, 160, 384.

giving the relation between the fraction of HD and the fraction of gas at equilibrium.

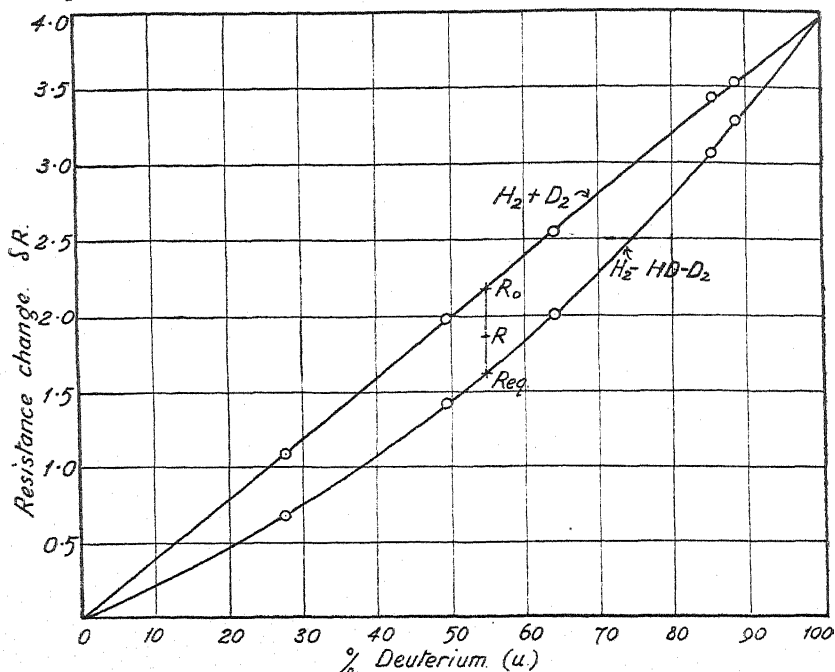


FIG. 1.—Resistance-Composition calibration curves.

The form of the gauge used has been described previously;¹ it consists of a platinum wire

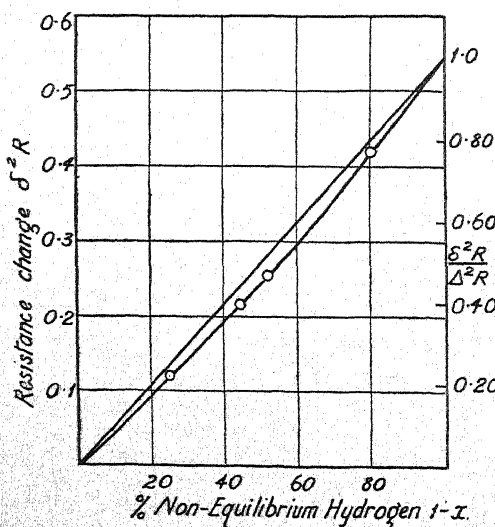


FIG. 2.—Graph of percentage of non-equilibrium hydrogen against resistance change.

consists of a platinum wire 0.015 mm. diameter, stretched axially down a tube 0.7 mm. wide; the tube is placed in a jacket through which water at 25° C. is pumped from a thermostat; the wire is heated to about 140° C. The gauge is operated at constant voltage and the resistance allowed to vary. Resistance-composition calibration curves for H₂-D₂ and H₂-HD-D₂ mixtures for this particular gauge are shown in Fig. 1. The resistance with hydrogen R_{H_2} is 88.36 Ω; δR is the change in resistance from the hydrogen value;

$$\Delta R = R_{D_2} - R_{H_2} = 3.99 \Omega.$$

When a mixture of hydrogen and deuterium, denoted by R_0 (Fig. 1), is brought to equilibrium its resistance falls from R_0 to R_{eq} ; the point R then represents a mixture of H_2 , HD and D_2 not at equilibrium. The resistance difference $R - R_{eq}$ is denoted by $\delta^2 R$ and $R_0 - R_{eq}$ by $\Delta^2 R$.

A calibration was made of the resistance change accompanying change in fraction of gas at equilibrium. This was done by making up a mixture of hydrogen and deuterium and dividing it up in two parts. The resistance value of one part was determined before and after bringing to equilibrium on a red hot nickel wire, giving points R_0 and R_{eq} . Samples of the non-equilibrated part were then added and resistance values determined. The calibration curve thus obtained is shown in Fig. 2.

It is of interest to calculate the form of the curve, assuming that the conductivity of a mixture is a linear sum of the conductivities of non-equilibrium and equilibrium hydrogen. In the analyser used in these experiments, the voltage was measured directly across the wire. Equation (3) of the previous paper then becomes, neglecting the resistance of the leads,

$$\frac{K_{eq}}{K} = \frac{R}{R_{eq}} \left(\frac{R - R_0}{R_{eq} - R_0} \right) \left(\frac{R + R_0}{R_{eq} + R_0} \right)^{0.77} \quad (2)$$

where K_{eq} and K are the conductivities of the equilibrium mixture and non-equilibrium mixture respectively.

With the small resistance difference observed, equation (2) can be expanded as a series:—

$$\begin{aligned} \frac{K_{eq}}{K} &= \left(1 + \frac{\delta^2 R}{R_{eq}} \right) \left(1 + \frac{\delta^2 R}{R_{eq} - R_0} \right) \left(1 + \frac{\delta^2 R}{R_{eq} + R_0} \right)^{0.77} \\ &= 1 + \delta^2 R \left(\frac{1}{R_{eq}} + \frac{1}{R_{eq} - R_0} + \frac{0.77}{R_{eq} + R_0} \right) \\ &\quad + (\delta^2 R)^2 \left(\frac{1}{R_{eq}(R_{eq} - R_0)} + \frac{0.77}{R_{eq}(R_{eq} + R_0)} \right. \\ &\quad \left. + \frac{0.77}{(R_{eq} - R_0)(R_{eq} + R_0)} - \frac{0.23 \times 0.77}{2 \times (R_{eq} + R_0)^2} \right). \end{aligned}$$

Taking the case when the deuterium content u is 50.5 per cent.

$$\begin{aligned} R_{non-eq} &= 90.40 \, \Omega & R_0 &= 66.80 \, \Omega \\ R_{eq} &= 89.85 \, \Omega & \Delta^2 R &= 0.549 \, \Omega. \end{aligned}$$

Inserting these we get

$$K_{eq}/K = 1 + 5.945 \times 10^{-2} \delta^2 R + 7.499 \times 10^{-4} (\delta^2 R)^2 \quad (3)$$

If $K_{non-eq} = 1.000$, $K_{eq} = 1 + y$, in arbitrary units, $K = 1 + xy$.

Substituting in equation (3), for complete non-equilibrium ($x = 0$), we get

$$\begin{aligned} y &= 5.945 \times 10^{-2} \times 0.549 + 7.499 \times 10^{-4} (0.549)^2 \\ &= 3.289 \times 10^{-2}. * \end{aligned}$$

* Cf. 3.994×10^{-2} calculated, from the results of Melville and Bolland, Table III.

Now

$$\begin{aligned}\frac{K_{eq}}{K} &= \frac{1+y}{1+xy} = \frac{1}{1 - \frac{1-x}{1+y} \cdot y} \\ &= 1 + \frac{y}{1+y}(1-x) + \left(\frac{y}{1+y}\right)^2(1-x)^2 + \dots \quad (4)\end{aligned}$$

and substituting in equation (3) we get

$$3.188(1-x) + 0.1018(1-x)^2 = 5.945\delta^2R + 0.075(\delta^2R)^2 \quad (5)$$

The calculated values shown in Table I. would indicate that the calibration curve should be practically a straight line, whereas

TABLE I.

x .	δ^2R calc.	δ^2R linear.	δ^2R obs.
0.2	0.436	0.437	0.419
0.5	0.271	0.272	0.245
0.8	0.108	0.109	0.094

the observed curve has a distinct dip. This effect can only be accounted for if the conductivity of the mixture is not a linear sum of the conductivities of its components; the effect observed here is in the same direction as that observed with

H_2 and D_2 , which has already been discussed in the foregoing paper.

A test of the calibration has been made by applying it to the reaction $H_2 + D_2 \rightleftharpoons 2HD$. An equimolecular mixture of hydrogen and deuterium was brought to equilibrium on a nickel wire at $120^\circ C$, and the rate of reaction observed by withdrawing and analysing samples. If b and b_{eq} are the fractions of HD present at time t and at equilibrium respectively, the rate of reaction is

$$db/dt = k(b_{eq} - b).$$

Integrating,

$$\ln(b_{eq} - b)/b_{eq} = kt,$$

or substituting in equation (1)

$$\ln(1-x) = kt.$$

The results obtained are given in Table II. and a graph of $\log_{10}(1-x)$ against t in Fig. 3. The graph is a very good straight line, thus confirming the accuracy of the calibration curve.

The shape of the calibration curve of Fig. 2 is the same for different deuterium contents, and in practice δ^2R is converted to δ^2R/Δ^2R ; the graph is then applicable to all deuterium concentrations.

In employing this gauge for the estimation of HD molecules, is therefore essential to calibrate it with known mixtures as the assumption of a linear calibration curve would lead to the introduction of a ten

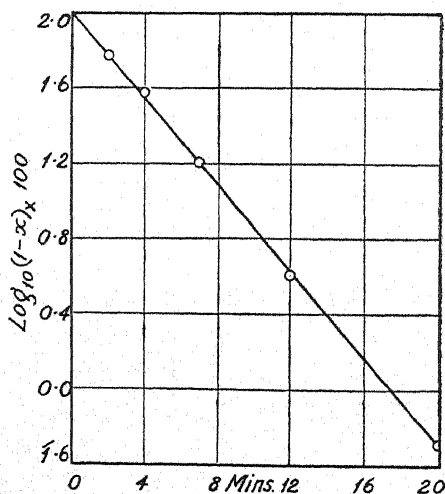


FIG. 3.—Course of equilibration of H_2 — D_2 with time.

per cent. error at least in the evaluation of velocity constants of the equilibration reaction.

TABLE II.

$t(\text{min.})$.	δ^2R .	δ^2R/Δ^2R .	$1-x) \times 100$.	$\text{Log}_{10} (1-x) 100$.
0	0.551	1.0	100	2.00
2	0.297	0.539	59.5	1.775
4	0.180	0.327	37.7	1.576
7	0.075	0.136	16.1	1.207
12	0.020	0.036	4.1	0.603
20	0.003	0.005	0.5	1.699

$$u = 49.7 \text{ per cent.}$$

The technique here described has been applied to following the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ on a nickel catalyst, both alone, and also when accompanied by exchange involving change in total deuterium content.

Summary.

A high pressure micro thermal conductivity method is described for the estimation of hydrogen deuteride molecules in mixtures of hydrogen and deuterium. The composition calibration curve is not linear as would be expected from the theory of the gauge.

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THE CONTINUOUS ABSORPTION SPECTRUM OF CHLORINE IN THE REGION 4000-5000 Å.

BY R. G. AICKIN AND N. S. BAYLISS.

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A careful investigation of the continuous absorption spectrum of chlorine at wave-lengths greater than 4000 Å. was undertaken for several reasons. There was the immediate interest in the possibility that the continuum, like that of bromine,¹ might be a complex one, a possibility that is evident both from the theory of the halogen spectra² and from the weak maximum that is present at about 4300 Å. in the results of

¹ A. P. Acton, R. G. Aickin and N. S. Bayliss, *J. Chem. Physics*, 1936, 4, 474.

² R. S. Mulliken, *Physical Rev.*, 1934, 46, 549; *J. Chem. Physics*, 1936, 4, 620.

³ H. v. Halban and K. Siedentopf, *Z. physik. Chem.*, 1922, 103, 71.

⁴ G. E. Gibson and N. S. Bayliss, *Physical Rev.*, 1933, 44, 188.

Halban and Siedentopf.³ Their experiments, unfortunately, were carried out at room temperature only, making it impossible to apply the method of temperature analysis to their data, while the range covered by Gibson and Bayliss⁴ in an investigation of the temperature coefficient of the absorption continuum does not extend to wave-lengths greater than 4275 Å.

Additional interest was lent to the problem by its bearing on the photochemistry of chlorine, and in particular on the photosynthesis of hydrogen chloride. In a great deal of the work on this important reaction, the active radiation has been of a wave-length greater than 4000 Å., and it is desirable therefore to have a correct interpretation of the continuum in this region, as well as accurate data relating to its temperature coefficient.

Experimental.

We used the method of photographic photometry that has been described already in connection with the previous investigations on chlorine and bromine.^{1, 4} Samples of chlorine were obtained (a) by the vacuum fractionation of chlorine prepared by heating dehydrated Merck's cupric chloride, and (b) by the vacuum fractionation of cylinder chlorine. The chlorine thus produced was used to fill the two silica absorption cells, 5 cm. and 20 cm. long. The concentration of the chlorine at each filling was determined by simultaneously filling an analysis bulb of known volume, which was then opened under slightly acid potassium iodide solution, the liberated iodine being estimated by titration against sodium thiosulphate. Several fillings, at pressures between 20 cm. and 70 cm., were used with each cell, a wide range of absorbing conditions being necessary because of the great variation in the absorption coefficient over our chosen range. The apparatus for handling the gas was made entirely of silica and Pyrex, and the few taps were lubricated with a mixture of graphite and concentrated sulphuric acid.

The source of light was a 60 watt projection lamp, and the Hilger medium spectrograph was fitted with the glass optical system for most of the measurements. The wire gauze screens were recalibrated, and their transmission factors were found to have changed but little since the investigation of the bromine spectrum. As before, wave-length calibrations were obtained from an arc between brass electrodes.

Since both bromine and bromine chloride absorb strongly in the region in which we worked, we tested the cupric chloride for the presence of bromide by means of the fluorescein reaction,⁵ using 25 per cent. chromic acid as the oxidising agent. Less than one mole of bromide to 10,000 of chloride was found, and any bromine impurity in the fractionated chlorine would, therefore, have a still lower concentration. Iodide cannot be regarded as a possible impurity in recrystallised cupric chloride.

Results.

We define the absorption coefficient, ϵ , by the relation: $\epsilon = (1/cd) \log_{10} (I_0/I)$, where c is the concentration of the gas in moles/litre, d is the length of the absorbing path in cm., and I_0 and I are the incident and transmitted intensities respectively. The values of ϵ given in Table I. are mean values derived from at least ten plates at each of the experimental temperatures. In Fig. 1, which includes the results of previous investigations, we have plotted $\log \epsilon$ over the range 2500 Å. to 5000 Å. at the temperatures 18° and 580° C. The values at wave-lengths greater

⁵ F. Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, (Leipzig, 1935), p. 277.

than that of the convergence of the $^3\Pi_{0+u} \leftarrow ^1\Sigma_g^+$ band system of chlorine (4785 Å.) are included as a matter of interest; but since the small dispersion of the spectrograph made it impossible to avoid the bands, our absorption coefficients in this region must be regarded as including both the band and the continuous absorption. Within the range of pressure and length of absorbing column that we used in our experiments, there was no evidence of failure of either Beer's or Lambert's laws.

Our experimental errors we believe to be less than 5 per cent., on the basis of the internal consistency of the measurements, and of the agreement with results of previous work. The experimental conditions made it difficult to equal the accuracy that was attained in the previous work on chlorine and bromine, since the absorption coefficients of chlorine and of the glass optical system of the spectrograph increase, and the intensity of the source decreases, as one approaches 4000 Å. from longer wavelengths. This resulted in a sharp decrease in the blackening on the plates,

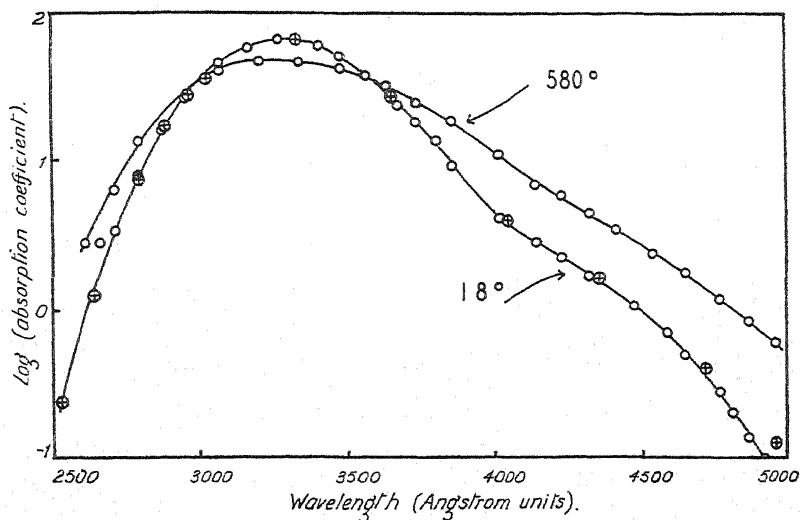


FIG. 1.—The continuous absorption spectrum of chlorine between 2500 and 5000 Å. at 18° and 580° C. Crossed circles—the results of Halban and Siedentopf. Open circles—results from Gibson and Bayliss and from Table I. Many experimental points have been omitted in order to keep the plot open.

which introduced difficulty into the photometer measurements. The difficulty was not overcome in the plates that were taken with the quartz optical system in the spectrograph, since the increased transparency was counterbalanced by the decrease in linear dispersion. A comparison of our results at room temperature with those of Halban and Siedentopf (see Fig. 1) shows that the latter authors obtained slightly higher values throughout the present range. In most cases, the difference is within the limit that we have set for our experimental error; but it becomes greater at the longer wave-lengths, particularly at 4960 Å. It is worth noting that Halban and Siedentopf used cylinder chlorine without purification in the range covered in this paper, and that the likely impurities in such chlorine are strongly absorbing ones. Jones and Spooner⁶ have measured absorption coefficients of chlorine at wave-lengths greater than 5000 Å., using an instrument with which they were able to avoid the bands. As might be expected, their values of ϵ are lower than ours. (Jones and

⁶ F. W. Jones and W. Spooner, *Trans. Faraday Soc.*, 1935, **31**, 811.

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Spooner state that their values are in agreement with those of Halban

and Siedentopf; but they seem to have compared their values of α , defined by $\alpha = (1/cd) \log_e (I_0/I)$, with Halban and Siedentopf's values of ϵ , defined as in this paper.)

If $\epsilon_{v''}$ is the absorption coefficient of molecules in the vibrational state v'' , and if a fraction $N_{v''}$ of the molecules are occupying that state, then

$$\epsilon = \epsilon_0 N_0 + \epsilon_1 N_1 + \epsilon_2 N_2 + \dots$$

Values of ϵ_0 and ϵ_1 were obtained from the data in Table I. by the method of temperature analysis that has been described by Gibson and Bayliss. They are shown in Fig. 2, plotted at intervals of 50 Å. from 4100 Å. onwards

TABLE I.

Wave-length (Å.).	Absorption Coefficients.					
	18° C.	183° C.	320° C.	464° C.	576° C.	709° C.
4023	4.18	6.5	8.2	10.2	11.1	12.4
4063	3.65	5.11	6.19	9.0	9.9	11.0
4144	2.87	3.86	5.09	6.55	6.85	9.1
4178	2.56	3.39	4.51	5.87	6.44	8.4
4227	2.24	2.90	3.82	5.08	5.88	7.5
4275	1.93	2.42	3.21	4.39	5.16	5.48
4326	1.71	2.10	2.73	3.77	4.49	5.32
4378	1.47	1.80	2.33	3.19	3.87	4.67
4415	1.30	1.61	2.07	2.87	3.48	4.29
4480	1.07	1.38	1.73	2.37	2.86	3.81
4539	0.85	1.13	1.36	1.96	2.44	3.30
4587	0.70	0.95	1.16	1.63	2.16	2.87
4651	0.50	0.76	0.97	1.27	1.78	2.50
4722	0.352	0.59	0.81	0.98	1.43	1.97
4767	0.279	0.50	0.70	0.90	1.18	1.76
4811*	0.206	0.42	0.61	0.77	1.03	1.58
4865	0.137	0.34	0.53	0.65	0.84	1.33
4919	0.101	0.28	0.45	0.51	0.74	1.16
4958	0.083	0.24	0.40	0.45	0.60	1.06
5017	0.059	0.19	0.34	0.35	0.46	0.93
5106	0.038	0.14	0.27	0.25	0.34	0.76
5220	0.029	0.09	0.18	0.19	0.25	0.58
5353	0.009	0.030	0.09	0.07	0.10	0.35
5432	0.002	0.02	0.06	0.04	0.04	0.26

* The values of ϵ at $\lambda > 4785$ Å. are in the region where the continuum is overlapped by the bands.

Discussion.

For the ϵ_1 component of a continuous absorption spectrum which involves only a single electronic transition, the theory of continuous absorption⁷ demands two maxima, which in the case of the main continuum of chlorine have been found to lie at 3780 Å. and 2980 Å.⁴ Hence the discovery of a third, weak maximum in ϵ_1 , that is to be seen in Fig. 2 at 4500 Å., is evidence that more than one electronic transition is involved in the continuous absorption of chlorine. This is confirmed by the rate at which ϵ_0 decreases, which seems to undergo a sudden change in the neighbourhood of 4000 Å. (Fig. 2), just as would be ex-

⁷ G. E. Gibson, O. K. Rice and N. S. Bayliss, *Physical Rev.*, 1933, 44, 193.

pected if the edge of the strong main continuum were overlapped by a weak continuous region with a maximum at about 4250 Å. Further evidence is supplied by Fig. 1. The hump on the long wave-length side of the continuum, which was observed in the results of Halban and Siedentopf and whose existence is confirmed by our work, becomes much less pronounced at higher temperatures. This is the effect that one would expect to be produced by overlapping continua belonging to different electronic transitions, since each continuum becomes wider and flatter at higher temperatures. (Compare the case of bromine.¹)

If there is a weak continuum with $\epsilon_0(\text{max.})$ at 4250 Å., there should be a maximum in ϵ_1 on either side. The long wave-length maximum is visible in Fig. 2 between 4300 and 4600 Å., and we believe the other one to be inseparable from the steeply rising ϵ_1 curve of the main continuum. We will denote the main continuum as *A*, ($\lambda_{\text{max.}} = 3300$ Å.), and the weaker one as *B*.

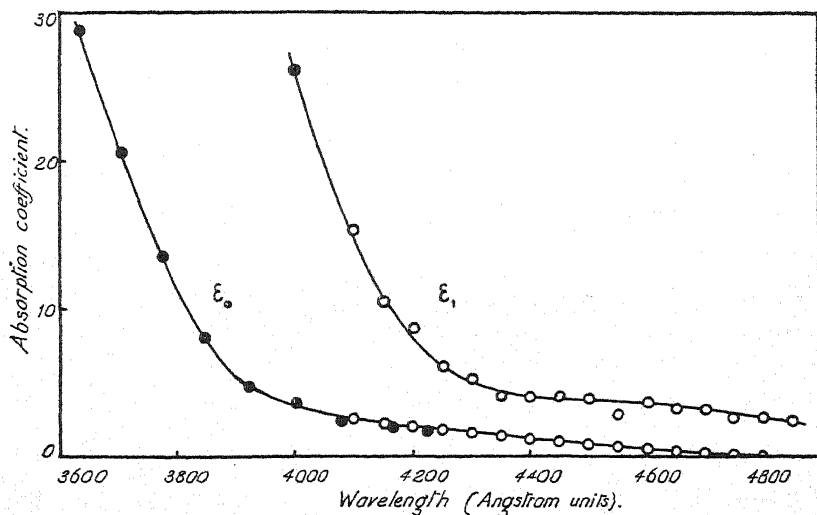


FIG. 2.—Values of ϵ_0 and ϵ_1 for chlorine between 3600 and 4850 Å. Full circles—results of Gibson and Bayliss. Open circles—values of present authors at intervals of 50 Å.

It has been shown by Mulliken² that there are two alternatives to be considered in assigning the observed continua to the electronic transitions that have been predicted theoretically. They are: (i) that *A* is a composite of the transitions $^1\Pi_u \leftarrow ^1\Sigma_g^+$ and $^3\Pi_{0+u} \leftarrow ^1\Sigma_g^+$, while *B* is due to $^3\Pi_{1u} \leftarrow ^1\Sigma_g^+$; (ii) that *A* is due to $^1\Pi_u \leftarrow ^1\Sigma_g^+$, while *B* is a composite of $^3\Pi_{0+u} \leftarrow ^1\Sigma_g^+$ and $^3\Pi_{1u} \leftarrow ^1\Sigma_g^+$. The evidence is rather in favour of (ii), which Mulliken considers to be more probable for chlorine than for bromine, where it is already well supported by the work of Bayliss⁸ and of Darbyshire.⁹ At first sight, evidence based on the Franck-Condon principle is unfavourable to (ii). The $U'(r)$ curve, calculated by Gibson, Rice and Bayliss⁷ for the upper state of the main continuum of chlorine was found to lie definitely above the Morse curve for $^3\Pi_{0+u}$, yet at the same time the maximum absorption

⁸ N. S. Bayliss, *Proc. Roy. Soc., A*, 1937, 158, 551.

⁹ O. Darbyshire, *ibid.*, 159, 93.

of the transition ${}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$ is predicted by the Morse curve to occur at about 3600 Å. If the Morse curve is correct, our B continuum can consist only of transitions to the ${}^3\Pi_{1u}$ state. However, on building up a more correct $U'(r)$ curve for ${}^3\Pi_{0+u}$ by the rather laborious graphical method described by Rydberg,¹⁰ using Elliot's data,¹¹ we found that the Morse curve is considerably in error, being too asymmetrical in the direction of large nuclear separations. The corrected curve, which we followed to the level $v' = 15$, indicated that the maximum absorption of the transition ${}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$ is near 4600 Å. (The dip at 4550 Å. in the ϵ_1 curve in Fig. 2 may, therefore, have the significance of being the accompanying minimum in ϵ_1 , although we had at first attributed it to experimental error.) Our calculation may be wrong by several hundred Å., not only because of the extrapolation from the level $v' = 15$, but also because few values of B_v'' are available for the ${}^3\Pi_{0+u}$ state of chlorine, the extrapolated values being uncertain because of the sharp discontinuity that Elliot found between the levels $v' = 8$ and $v' = 11$. However, our calculation makes it certain that the transition ${}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$ is to be found in the B continuum, in accordance with explanation (ii).

It is planned to discuss certain photochemical consequences of this work in a later paper, since the above assignment leads to the result that photodissociation of chlorine molecules in the region of the main continuum produces normal (${}^2P_{1\frac{1}{2}}$) atoms only, and not, as has been assumed hitherto, half in each of the states ${}^2P_{\frac{1}{2}}$ and ${}^2P_{3\frac{1}{2}}$.

Summary.

Values of the absorption coefficient of chlorine in the spectral region 4000-5400 Å. are recorded at six temperatures from 18° to 709° C. A temperature analysis of the results reveals that the continuous absorption spectrum of chlorine contains two components, designated as A and B . A has $\epsilon_{\max} = 66$ at 3300 Å., and is due to the transition ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$, which leads to dissociation into normal atoms. B is much weaker, with $\epsilon_{\max} \approx 1$ at about 4250 Å., and is a composite of the transitions ${}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ and ${}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$ (corresponding to the visible bands), producing dissociation into $\text{Cl}({}^2P_{1\frac{1}{2}}) + \text{Cl}({}^2P_{1\frac{1}{2}})$ and $\text{Cl}({}^2P_{1\frac{1}{2}}) + \text{Cl}({}^2P_{\frac{1}{2}})$ respectively.

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¹⁰ R. Rydberg, *Z. Physik.*, 1931, **73**, 376.

¹¹ A. Elliot, *Proc. Roy. Soc., A*, 1930, **127**, 638; W. Jevons, *Report on Band Spectra* (The Physical Society, 1932), p. 280.

THE CONTINUOUS ABSORPTION SPECTRUM OF CHLORINE AND THE PHOTOSYNTHESIS OF HYDROGEN CHLORIDE.

BY N. S. BAYLISS.

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Recent work,^{1, 2, 3} has led to the following interpretation of the continuous absorption spectrum of chlorine. The continuum, which is found to extend well into the region of band absorption, is made up of several components. The region of strong absorption, lying roughly between 4100 and 2500 Å., is due to the transition ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$, and is accompanied by photodissociation into normal (${}^2P_{1/2}$) chlorine atoms. Overlapping this, there is a region of much weaker absorption extending from about 4000 to well beyond 5000 Å., that is a composite of the transition ${}^3\Pi_{0+u} \leftarrow {}^1\Sigma_g^+$, (dissociating into $\text{Cl}({}^2P_{1/2}) + \text{Cl}({}^2P_{1/2})$), and the transition ${}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$, that gives normal atoms. In the light of this work and of the high temperature coefficient of absorption that has been found at the longer wave-lengths,³ it has become possible to explain certain of the puzzling features of the photosynthesis of hydrogen chloride, and in part to simplify its interpretation.

The Reaction at Wave-lengths Greater than 4785 Å.

It has been well established that the reaction can be caused by radiation of longer wave-length than the convergence of the visible band system of chlorine,^{4, 5} and it has been suggested that either or both of two primary processes may be effective in this region; namely, the dissociation of chlorine molecules into atoms, and the initiation of chains by excited chlorine molecules.^{4, 6} The work of Jones and Spooner² makes it clear that continuous absorption accompanies the band absorption to wave-lengths much greater than 5000 Å., and Craggs and Allmand,⁴ in their discussion of the reaction at 5460 Å., have pointed out that the hitherto assumed dissociation of chlorine molecules into $\text{Cl}({}^2P_{1/2}) + \text{Cl}({}^2P_{1/2})$ cannot occur at this wave-length unless the molecules are in vibrational states with $v'' \geq 6$. To overcome the difficulty that so few molecules are in such states (< 0.00001 per cent. at 18° c.), they suggested that normal chlorine molecules with $v'' \geq 3$, when absorbing light of this wave-length, could dissociate into normal atoms by means of a radiationless transition from the excited state ${}^3\Pi_{0+u}$ to one of the predicted states ${}^1\Pi_u$ and ${}^3\Pi_{1u}$. Such a process seems improbable, since the band absorption of light of wave-length 5460 Å. by molecules with $v'' = 3$ produces molecules in a vibrational state

¹ G. E. Gibson and N. S. Bayliss, *Physical Rev.*, 1933, 44, 188.

² F. W. Jones and W. Spooner, *Trans. Faraday Soc.*, 1935, 31, 811.

³ R. G. Aickin and N. S. Bayliss, *This vol.*, page 1333.

⁴ H. C. Craggs and A. J. Allmand, *J. Chem. Soc.*, 1936, 241.

⁵ E. Hertel, *Z. physik. Chem., B*, 1932, 15, 325.

⁶ K. F. Bonhoeffer and P. Hartek, *Grundlagen der Photochemie* (Dresden, 1933), p. 246; N. Semenov, *Chemical Kinetics and Chain Reactions* (Oxford, 1935), p. 109.

of ${}^3\Pi_{0+u}$ that shows no evidence of blurred rotational structure. In fact, this level is among the few whose rotational structure was analysed by Elliot.⁷ The work of Aickin and Bayliss,³ however, has shown that the continuous absorption in this region is due at least partly to transitions to the ${}^3\Pi_{1u}$ state, which dissociates into normal atoms. It is therefore unnecessary to postulate a radiationless transition in order to understand how reaction chains can be started by chlorine atoms that are produced by absorption at 5460 Å. It is not precluded by this result that the second mechanism, the initiation of chains by excited molecules, may also take part in the reaction at 5460 Å. This question will be discussed later in connection with the quantum yield of the reaction.

The Temperature Coefficient of the Reaction.

In the many investigations of the temperature coefficient of the reaction,^{4, 5, 8} there has been general agreement that the temperature coefficient is practically independent of wave-length at wave-lengths less than 4785 Å.; but that it increases at wave-lengths greater than this. Although several authors have referred to the possibility that the absorption coefficient of chlorine varies with the temperature, only Potts and Rollefson⁸ appear to have deliberately measured the temperature coefficient of the reaction at a wave-length where the absorption coefficient was known to be independent of the temperature.

The correction for the temperature coefficient of the absorption will depend on the fraction of the incident light that is being absorbed in the particular experiment. Since $I_{abs.} = I_0(1 - 10^{-\epsilon a})$, the amount of light absorbed is proportional to ϵ if $I_{abs.}/I_0$ is small, but is independent of ϵ if $I_{abs.} \approx I_0$. To take an example of the effect of correcting for the temperature coefficient of ϵ , Craggs and Allmand⁴ measured rates of the reaction at 57° and at 18° C. in circumstances where $I_{abs.}/I_0$ was small. They found the temperature coefficients of the rate of reaction to be 1.3 at 4360 Å. and 1.76 at 5460 Å. Now by using the reasonably accurate assumption that ϵ varies linearly with temperature in the range between 18° and 180° C., it can be found from the results of Aickin and Bayliss³ that at 18° and 57° C., $\epsilon = 1.47$ and 1.55 respectively at 4378 Å., and = 0.002 and 0.006 at 5432 Å. Using these figures to correct the results of Craggs and Allmand, it is found that the correction at 4360 Å. is negligible, and that at 5460 Å. the temperature coefficient of the reaction is reduced to a value identical with that at shorter wave-lengths. The energy of activation of the reaction is therefore independent of wave-length, and the apparent increase at longer wave-lengths was due, as suggested by Craggs and Allmand, to the high temperature coefficient of ϵ in this region.

The Variation of Quantum Yield with Wave-length.

The question of the mechanism of the reaction at wave-lengths greater than 4785 Å. can be discussed conveniently in connection with the quantum yield. Semenov⁹ has shown that if the reaction in this region is solely due to chains that start from excited chlorine molecules,

⁷ A. Elliot, *Proc. Roy. Soc., A*, 1930, **127**, 638.

⁸ J. C. Potts and G. K. Rollefson, *J. Amer. Chem. Soc.*, 1935, **57**, 1027.

⁹ N. Semenov, *loc. cit.*,⁶ p. 112.

the quantum yield should be about $1/9$ of that at shorter wave-lengths. In qualitative agreement with this, it has been reported that the quantum yield at wave-lengths greater than 5000 Å. is 0.5 to 0.3 of its value in the purely continuous region.^{4, 10} However, a consistent explanation of the facts can be obtained if it be assumed that, no matter what the wave-length of the exciting radiation, only one primary process need be considered, namely the formation of chlorine atoms by photodissociation. It has been shown above that the continuous absorption that extends into the band region is able to produce chlorine atoms, and that the corrected energy of activation indicates that the mechanism of the reaction is independent of wave-length. With respect to the quantum yield, it must be remembered that it has almost invariably been calculated on the basis of the absorption coefficients given by Halban and Siedentopf.¹¹ It has been shown³ that at wave-lengths greater than 4785 Å., these values include both band and continuous absorption, which are difficult to separate without an instrument of high dispersion such as that used by Jones and Spooner,² whose values for the absorption coefficient of the continuum alone are about 0.4 of those of Halban and Siedentopf.³ If it is assumed that the reaction in this region is caused by only that part of the absorption that is continuous, the observed quantum yield must be increased to a value practically the same as that at wave-lengths less than 4785 Å. Hence the phenomena associated with the occurrence of the reaction in the "band" region can be explained on the assumption that the primary process is the same as that in the "continuous" region, a result that is attractive on account of its simplicity.

In addition to the apparent variation of quantum yield with wave-length that is discussed in the preceding paragraph, Craggs and Allmand⁴ have reported that whereas the quantum yield is practically constant in the region 4785-4000 Å., it appears to decrease slightly at still shorter wave-lengths. The effect is observed only at low chlorine pressures (1.7 mm.), and the larger variations that were reported in previous papers of the same series¹² have not been confirmed by their most recent work. It is interesting that the region in which they find the maximum value of the quantum yield is the only one in which photodissociation produces both normal and excited chlorine atoms, since it includes the limits within which the transition $^3\Pi_{0+u} \leftarrow ^1\Sigma_g^+$ is important. At wave-lengths less than 4000 Å., practically only normal atoms are produced. Any difference in reactivity between chlorine atoms in the $^2P_{3/2}$ and $^2P_{1/2}$ states could scarcely affect the length of the reaction chains, since the difference would exist only for the first "link" of the chain. One might expect a difference in their respective efficiencies in starting chains, or in reacting with the inhibitors that apparently cannot be banished from the reaction system. Rollefson and Potts¹³ have actually shown that normal chlorine atoms react much more rapidly with the inhibitor ICl than do excited ($^2P_{3/2}$) atoms. In addition, a variation in quantum yield caused by such differences would be expected only at low gas pressures, as found by Craggs and Allmand, since excited atoms would probably be deactivated fairly rapidly by collision.¹⁴

¹⁰ K. F. Bonhoeffer and P. Harteck, *loc. cit.*⁶

¹¹ H. v. Halban and K. Siedentopf, *Z. physik. Chem.*, 1922, 103, 71.

¹² J. B. Bateman and A. J. Allmand, *J. Chem. Soc.*, 1934, 157; A. J. Allmand and E. Beesley, *ibid.*, 1930, 2709.

¹³ G. K. Rollefson and J. C. Potts, *J. Chem. Physics*, 1933, 1, 400.

¹⁴ G. K. Rollefson, *private communication*.

Summary.

Various features of the photosynthesis of hydrogen chloride (in the absence of oxygen) have been discussed in the light of recent work on the continuous absorption of chlorine. It is shown that the only primary process that need be assumed is the photodissociation of chlorine molecules into atoms, and that in accordance with this, the quantum yield, the temperature coefficient, and the energy of activation of the reaction are practically independent of the wave-length of the exciting radiation. The slight change of quantum yield with wave-length, that has been observed at low gas pressures only, is interpreted in terms of a difference between $\text{Cl}(^2P_{3/2})$ and $\text{Cl}(^2P_{1/2})$, either in starting reaction chains or in reacting with inhibitors.

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A CRITICAL STUDY OF SOME RECENT INVESTIGATIONS ON THERMAL CHANGES IN SIMPLE ORGANIC COMPOUNDS.

BY MORRIS W. TRAVERS.

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While it is beyond question that we must rely very largely on the results of gas reactions for our knowledge of the mechanism of chemical processes, in no branch of chemistry are the reliability of experimental data, and the validity of the conclusions drawn from them, more open to question. This is particularly the case in the branch of the subject in which I am interested, the thermal decomposition of simple organic compounds. So far as the experimental work is concerned, the reason for this is largely that it is difficult and laborious; and this has inclined investigators to use simple and rapid methods, which may be described as yielding only a first approximation to the truth.

I must begin by calling attention to an important matter which is generally overlooked. There has been a general failure to recognise the fact that it is the initial part of a chemical process which is of the greatest interest, and which should be the subject of the most careful study. A very large number of experiments have yielded results which are said to be represented by equations, sometimes of bimolecular, but more generally of unimolecular form. Detailed investigation shows, however, that the initial portion of the x/t graphs bend towards the x -axis. This is often referred to as an *induction period*, sometimes with the implication that it can be ignored, while the second portion of the graph may, to quote Semenov¹ "be more or less accurately interpreted from the standpoint of the unimolecular or bimolecular law. Such interpretations, however, hardly present any interest, and certainly cannot serve for a better understanding of the reaction, until we have answered the principal question as to why and how the reaction velocity increases from the beginning." Besides this, it has been the too common practice to allow

¹ Semenov, *Chemical Kinetics and Chain Reactions*, 1935, p. 386.

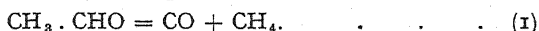
a reaction to proceed to the end, and then, from a study of the end products, to attempt to correct the results so that they conform to what is supposed to be a simple law governing the main reaction.

On the experimental side the results fall mainly under two headings. By far the greater number of investigations have involved the observation of changes of pressure at constant volume and constant temperature, the observations being supplemented by a few analyses. In a certain number of cases, mainly in my own laboratory, the process has been followed by making detailed analyses of the contents of reaction vessel after definite time intervals.

I propose to discuss the results obtained from the study of the thermal decomposition of a few common compounds, and the conclusions which have been deduced from them.

Acetaldehyde.

The study of the thermal decomposition of acetaldehyde illustrates the diversity of the results and conclusions of a number of workers. The first investigations of importance were those of Hinshelwood and his co-workers. In 1926 Hinshelwood and Hutchinson² studied the decomposition process between 430° and 590°, and at initial pressures between 60 and 480 mm. of mercury in silica apparatus. Analysis of the products indicated that the main process was represented by the equation,



The rate of the reaction was followed by observing changes in pressure at constant volume. The results of only one series of observations are given in the paper (518° and 363 mm.) and these show that the x/t graph bends continuously towards the t -axis. The authors concluded that the process was "practically homogeneous," though actually packing the reaction tube with powdered silica appeared to increase the velocity of reaction by 30 per cent. Since the value of $t_{1/2}$, the *half-life period*, increased linearly with the initial pressure, the authors concluded that the process was bimolecular. The critical increment was found to be 45.5 K. cals., "and the rate of reaction could be calculated from kinetic considerations, and was in close agreement with experiment."

In a second paper Fletcher and Hinshelwood³ pointed out that though the $t_{1/2}/P_0$ graphs were linear, they did not pass through the origin. To explain this fact they extended the investigation over a range from 0.2 to 1100 mm. of mercury. The $t_{1/2}/P_0$ graphs now showed very sharp breaks, which, they say, "can only be explained by the theory that the acetaldehyde molecule can be activated in a limited number of distinct ways, and that different activated states can be associated with different transference probabilities. There are then several virtually independent quasi-unimolecular decompositions for the same chemical reaction. The energy of activation for the mode of reaction predominating at low pressures is higher than for the greater pressures."

A little later Hinshelwood, Fletcher, Verhoek, and Winkler⁴ extended the investigation to the comparative study of the behaviour of formaldehyde, acetaldehyde, propionic aldehyde, and trichloroacetaldehyde. Only in the case of the first named is the $t_{1/2}/P_0$ graph linear, passing through the origin.

It may be observed that the thermal decomposition of formaldehyde into carbon monoxide and hydrogen,⁵ is probably unique; for, apart from

² Hinshelwood and Hutchison, *Proc. Roy. Soc. A*, 1926, **111**, 380.

³ Fletcher and Hinshelwood, *ibid.*, 1933, **141**, 41.

⁴ Hinshelwood, Fletcher, Verhoek and Winkler, *ibid.*, 1934, **146**, 32.

⁵ Fletcher, *ibid.*, 1934, **146**, 357.

the fact that this compound undergoes slight polymerisation, which is probably a surface process, it seems to be the only known case in which a simple organic compound undergoes direct thermal decomposition in accordance with the bimolecular law.

At this stage criticisms of these researches were put forward by Rice and Herzfeld⁶ and by myself and my co-workers,⁷ and in reply to these criticisms Winkler and Hinshelwood published a further short paper,⁸ containing the results of a "more detailed study of the effect of surface, and dimensions of the reaction vessel, on the thermal decomposition of acetaldehyde vapour. "They confirmed their previous conclusion that the process proceeds according to equation (1), and they found no evidence that it was appreciably heterogeneous, or that it depended upon a chain mechanism. They also restated the view that pressure increase gives a reliable measure of reaction rate.

Rice and Herzfeld⁶ consider that the results of Hinshelwood and his colleagues represent a 1.5 order reaction, which can be explained by means of a chain mechanism, though they admit that there is no evidence supporting this conclusion, and that the presence of free radicals at the temperature at which the experiments were carried out has not been demonstrated. Letort⁹ from these results, and from his own investigations came to the same conclusion. In a series of papers Sachsse and Patat¹⁰ show that the concentration of free radicals in the systems studied by Rice and Herzfeld is too small to account for the phenomena.

I shall refer to the influence of ethylene oxide and of azo-methane on the decomposition of acetaldehyde later.

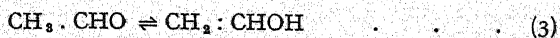
The work on acetaldehyde carried out in my laboratory is described in two papers.^{11, 12} The method of investigation, called the method of detailed analyses, consists of heating a known quantity of the reactant in a silica reaction tube for a known time to a known temperature, and then analysing the products. As each point on an x/t graph involves a day's work, the method is laborious.

The experiments showed in the first place that methane and carbon monoxide are not the sole products of the thermal decomposition of acetaldehyde, though the reaction represented by equation (1) predominates in an empty tube. In a packed tube an alternative process predominates,



However, the overall rate of decomposition of acetaldehyde is independent of whether the tube is packed or not. This suggests that, contrary to the view of Hinshelwood and his colleagues, a single activation process may give rise to *paired products*.

In the second place the x/t graphs do not curve towards the t -axis, but towards the x -axis, the decomposition process being self-accelerated. This self-acceleration continues up to a point at which the graphs show sharp breaks, indicating a sudden slowing down of the reaction. While the rate of the overall reaction is otherwise independent of surface the conditions which give rise to the break point are dependent on the nature of the surface, and are influenced by the addition of gases to the acetaldehyde vapour. It is suggested that the apparent self-acceleration of the thermal process is due to the fact that the whole process involves several stages. The first stage, called the *background reaction*, involves a change represented by,



⁶ Rice and Herzfeld, *J. Am. Ch. Soc.*, 1934, **56**, 284.

⁷ Travers, *Proc. Roy. Soc. A*, 1934, **146**, 248.

⁸ Winkler and Hinshelwood, *ibid.*, 1935, **149**, 355.

⁹ Letort, *Thesis*, Paris, 1937.

¹⁰ Sachsse and Patat, *Z. physik. Chem. B*, 1935, **31**, 79, 87, 105.

¹¹ Seddon and Travers, *Proc. Roy. Soc. A*, 1936, **156**, 234.

¹² Travers, *Trans. Faraday Soc.*, 1936, **33**, 735.

A second stage involves reaction between the molecular species represented in the *background reaction*, leading to the formation of an unstable intermediate compound. This, if it remains long enough in the gas phase, decomposes into methane and carbon monoxide; if, however, within its life period, it strikes a surface, it is adsorbed, and decomposes yielding propylene, carbon monoxide, and water vapour.

It is clear, therefore, that there are three totally different views about this much discussed substance, and the differences relate to the validity both of the experimental data, and of the conclusions to be drawn from them.

The Simple Hydrocarbons.

An enormous amount of work has been devoted to the study of the thermal decomposition of the simple hydrocarbons, but the greater part of it relates to attempts to elucidate the mechanism of the processes involved by studying the products of reaction from the standpoint of organic chemistry. Very little of it is complete and quantitative.

A considerable amount of attention has been paid to the study of the reversible system,



but as the process is catalysed by a silica surface, all that has resulted is the evaluation of some approximate temperature coefficients. Rice and Herzfeld have, indeed, built up ⁸ an elaborate mechanism for the reversible process itself, and for the formation of methane and a 4-carbon hydrocarbon from ethane, but, though they state that the later process is unimolecular, it is not clear as to the facts on which this statement is based. I have referred to the work of Sachsse and Patat ¹⁰ discounting the idea that free radicals can be present at a concentration sufficient to account for the phenomena which are described.

The work carried out in my laboratory seems to indicate that the only homogeneous reactions, if indeed they are homogeneous, in which ethane and ethylene take part independently, are those indicated by equation (4) above. The polymerisation of pure ethylene is mainly, if not entirely a surface reaction. Pease ¹³ found that ethylene polymerised between 350° and 500°, and between 2 and 9 atmospheres pressure, in a copper vessel, the process following a bimolecular law. Hockin and I, experimenting ¹⁴ at 360°, found rates of polymerisation in silica apparatus, very much slower than were found by Pease. ¹³ Also at 590° we found that the initial rate of polymerisation of pure ethylene was very small, a fact which Pearce and I (p. 326) ¹⁵ found very disturbing, as we then believed that the condensation process followed a square law. More recent work in my laboratory shows that this view is incorrect. ¹⁶ I shall return to this point later.

The thermal decomposition of ethane and ethylene was first studied in my laboratory about five years ago, and it was observed that in the case of pure ethane, the rate of formation of methane and of condensation products, expressed in terms of 2-carbon hydrocarbon disappearing, were represented by graphs which curved initially towards the x -axis, and then showed breaks indicating a sudden slowing down of the process ¹⁷ (Fig. 1). It was found however, that if, instead of working with pure ethane, ethane-ethylene-hydrogen equilibrium mixtures were used, the processes ceased to be self-accelerated, the x/t graphs bending continuously towards the t -axis, and the breaks did not appear. Following this initial survey of the problem, an extensive research was carried out in the region of temperature 500°-600°, and with a wide range of equilibrium mixtures. ¹⁵ An

¹³ Pease, *J. Am. Ch. Soc.*, 1931, 631.

¹⁴ Travers and Hockin, unpublished.

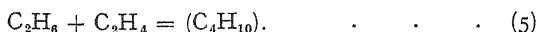
¹⁵ Travers and Pearce, *J. Soc. Ch. Ind.*, 1937, T. 321.

¹⁶ Travers, *Trans. Faraday Soc.*, 1936, 33, 236.

¹⁷ Travers and Hockin, *Proc. Roy. Soc., A*, 1932, 136, 1.

attempt was made to explain the formation of methane and condensation products on the assumption that they arose from different activation processes.

The work on acetaldehyde already described, which led me to the conclusion that *paired products* might result from a single activation process, and a survey of other investigations in progress in my laboratory, suggested that the following mechanism might account for the thermal changes in the simple hydrocarbons.¹² In the case of ethane the process is initiated by primary decomposition, of the hydrocarbon and formation of ethylene and hydrogen in accordance with equation (4). This is the background reaction in this process. The second stage involves the reaction,



It must be admitted that the explanation is open to objection, as is the alternative that the initial change involves the formation of a C_3 -complex

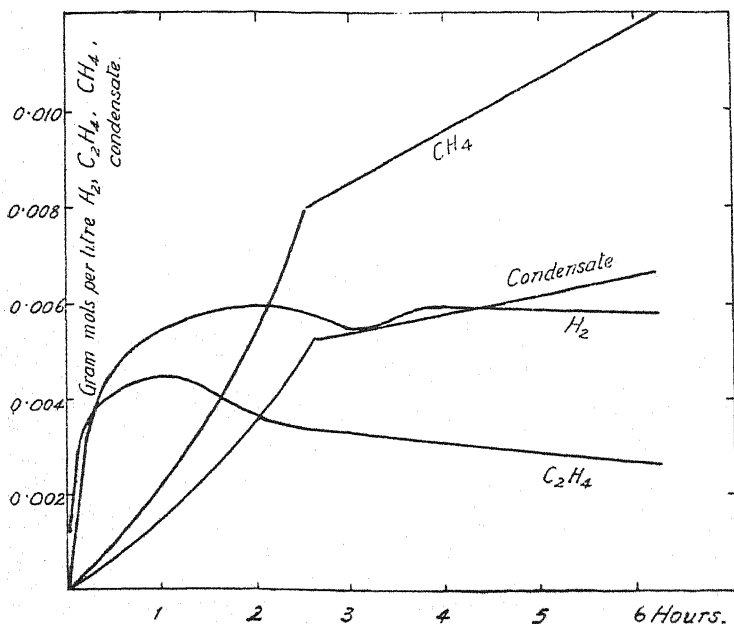


FIG. 1.

and methane or a C-radical. The product of this process, which is very unstable, decomposes in presence of hydrogen yielding, alternatively, methane or a condensation product. Since the decomposition of the intermediate is very rapid, the sum of the methane and condensate, expressed as 2-carbon hydro-carbon decomposed, gives a measure of the rate of formation of the unstable intermediate, and this is proportional to the product of the concentrations of the ethane and of the ethylene.

This rule holds exactly only under the condition that the initial composition of the equilibrium mixture, and the rate of the reaction, is such that equilibrium in the system is maintained without the operation of the background reaction to any great extent (p. 741),¹² since the background reaction has some influence on the rate of the bimolecular process. However, it does hold over so wide a range of experimental conditions, so that the explanation may be regarded as a plausible one, and one which at least represents the facts.

The results of a study of the thermal changes in propane-propylene-hydrogen equilibrium mixtures lends strong support to the conclusions based upon the study of the ethane-ethylene-hydrogen equilibrium mixtures.¹⁸

To return to the problem of the thermal decomposition of pure ethane. The changes are represented by the graphs in Fig. 1, which represent,

The rate of formation of methane,
The rate of formation of condensate,
The rate of formation of ethylene,
The rate of formation of hydrogen.

Since the concentration of ethane and of ethylene are known at any moment, it should be possible to calculate the rate of formation of (Methane + Condensate) from the data obtained from the study of the ethane-ethylene-hydrogen equilibrium mixtures. The observed rate of formation of (Methane + Condensate) is now always a little greater than calculated rate (p. 744),¹² and the difference increases to a maximum at the break-point, when it falls to zero. The exact cause of this difference is difficult to determine, particularly for the reason that, in this case, the background reaction is at least partly heterogeneous. It may possibly be accounted for by the fact that the energy of the background reaction is partly used up in increasing the concentration of hot molecules in the gases which take part in bimolecular process. The effect seems to disappear in a packed tube (p. 532).¹⁵

The processes which, it is suggested, are involved in the thermal decomposition of acetaldehyde and the simple hydrocarbon may be expressed in general form by the equations,



Equation (6) is the background reaction. The second process results in the formation of an intermediate (AB)', which is an unstable chemical compound, a transition state (AB) possibly intervening. The unstable intermediate decomposes very rapidly in these cases yielding one or more sets of products, so that we are actually measuring the rate of the bimolecular process,



Ethylene Oxide and Acetaldehyde.

It has been suggested that since acetaldehyde is formed during the thermal decomposition of ethylene oxide, it may possibly be an intermediate in the process which yields, as main products, methane and carbon monoxide. Seddon and Travers¹¹ considered this unlikely since no 3-carbon hydrocarbon was formed when ethylene oxide decomposed, and this compound is always a product of the thermal decomposition of acetaldehyde. Fletcher¹⁹ first observed that the addition of ethylene oxide to acetaldehyde increased the rate of formation of methane and carbon dioxide; and though he did not prove that these products were derived from the acetaldehyde, he suggested that the decomposition of acetaldehyde was catalysed by the ethylene oxide.

The reaction has been carried a stage further by Silcocks and myself.²⁰ With a mixture of acetaldehyde and ethylene oxide in equimolecular proportion at an initial pressure for each of 0.012 gram mols. per litre, and at 360° C., an isothermal was determined, the quantities of methane and carbon monoxide formed and of acetaldehyde changed being measured.

¹⁸ Travers, *Trans. Faraday Soc.*, 1937, **33**, 751.

¹⁹ Fletcher, *J. Am. Ch. Soc.*, 1936, **2**, 135.

²⁰ Silcocks and Travers unpublished.

The results showed that the rate of formation of methane and carbon monoxide were practically exactly equal, and also practically exactly equal to the quantity of acetaldehyde disappearing. The form of the graph showed that the process was initially self-accelerated, and there are three marked discontinuities. It has a striking similarity to the graph representing the secondary process which arises when the thermal decomposition of dimethyl ether into methane and formaldehyde is suppressed by the action of nitric oxide.

It is evident that the products are derived substantially from the acetaldehyde, but by a process which is essentially different from the normal thermal decomposition at the same temperature, for in this case the carbon monoxide is always in excess, on account of the operation of the alternative decomposition process. This very interesting phenomenon does not really throw any light on the mechanism of the normal thermal decomposition of acetaldehyde, any more than does the similar behaviour of azomethane.²¹ Fletcher¹⁹ suggests that the decomposition of ethylene

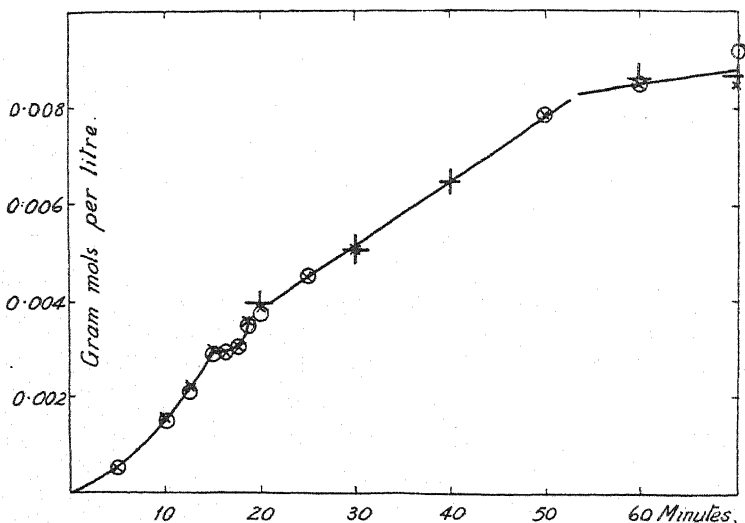


FIG. 2.

oxide gives rise to methylene radicals and formaldehyde, the methylene radicals reacting to form methyl radicals, by which a chain mechanism is initiated. The suggestion is a little far-fetched.

It is not impossible that there is something in the analogy with the methyl ether-nitric oxide reaction, which I shall refer to later. We expect to find that, in presence of acetaldehyde, the decomposition of ethylene oxide itself is slowed down, accompanying the acceleration of the decomposition of the acetaldehyde.

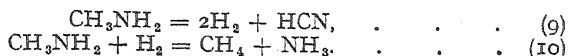
Methylamine.

The results of the study of the thermal decomposition of methyl amine between 500° and 600° in my laboratory has led to results which are different from those obtained by others. When we took up the subject Eméleus and Jolley²² had just published the results of an investigation, which had

²¹ Sukman and Allen, *J. Am. Ch. Soc.*, 1934, 1251.

²² Einstein and Jolley, *J. Chem. Soc.*, 1935, 929.

led them to the following conclusions. The decomposition process involves two reactions, represented by the equations,



The first process was unimolecular, and homogeneous, and the second heterogeneous. They were related through the operation of a chain mechanism.

We spent a very long time in attempting to eliminate the disturbing effect of surface, and possibly of impurities in the methyl amine, but with little success. It seemed practically impossible to obtain reproducible results, but our experiments led to certain important conclusions. First of all, if the reactions are regarded as independent, they are represented

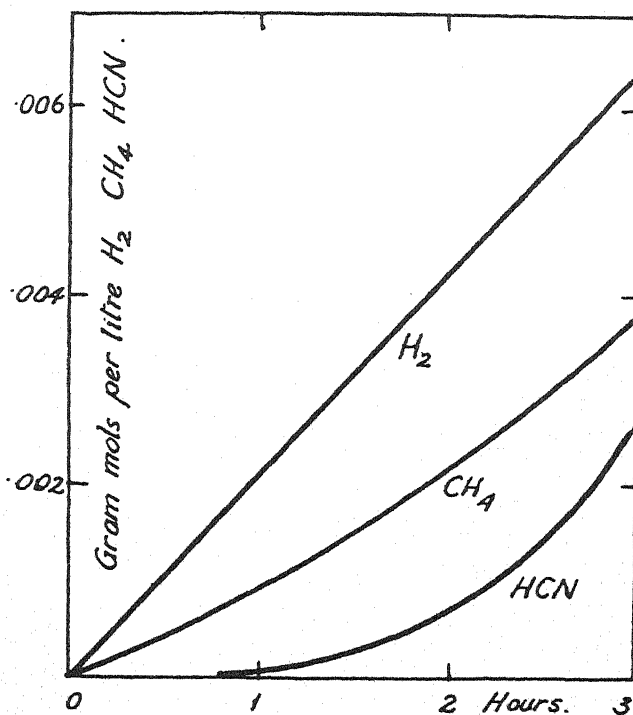


FIG. 3.

by graphs which indicate self-acceleration. The processes are not unimolecular. Secondly, the rates of the two processes tend to equality; and lastly the second process is unaffected by the addition of hydrogen to the methyl amine. These results suggested that the thermal process involved the formation of an intermediate compound, and that the transfer of hydrogen was internal.

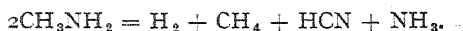
Up to this point, our experiments had been conducted by measuring the quantities of hydrogen and methane produced in successive increasing intervals. We now set out to study the changes over the initial short period more carefully, and particularly the rate of formation of hydrocyanic acid. A series of experiments were carried out at 520°, and at an initial concentration 0.0265 gram mols. per litre of methyl amine. The hydrocyanic acid was measured colorimetrically by a modification of the

method of Johnson,²³ which proved to be very accurate. In Fig. 3 the graphs show the rates of formation of hydrogen, methane, and hydrocyanic acid for the first three hours, and it will be noticed that in one hour less than 0.00001 gram mols. per litre, in a 60 c.c. reaction tube, which could be detected, but not measured, was formed. The rate of formation of the hydrocyanic acid after an hour becomes rapid.

The following experiment was then carried out. After heating for one hour, using the apparatus of Seddon and Travers (p. 241),¹¹ the reaction tube being cooled in liquid air the methane and hydrogen were pumped off. The reaction tube was now cooled in solid carbon dioxide and alcohol, and connected with a bulb cooled in liquid air, with which it was allowed to remain in communication for twenty-four hours. In this way all unchanged methyl amine and ammonia was removed from the reaction tube, to which a new stem was sealed, without allowing it to warm up. It was then exhausted and returned to the furnace at 520° for a further period of twenty-four hours.

The methane and hydrogen formed during this second period were then pumped off. The reaction tube was washed out with alkali, and the hydrocyanic acid, and in one case also the ammonia, was estimated. It was now found that the hydrogen, methane, and hydrocyanic acid formed during this period of reheating were very closely in equimolecular quantities. The one estimation of the ammonia gave about 0.8 of an equivalent.

It is quite evident from these experiments that there is a process, probably involving two molecules of methyl amine, the overall change in which can be represented by the equation,



So far as our experiments have proceeded, it seems to be quite clear that a compound is formed which certainly yields the first three of the products, and which, in that case, must have the formula $\text{C}_2\text{H}_7\text{N}$, which is non-volatile at -80° , and is relatively stable at 520° . It is easy to write a variety of formulæ to correspond to this composition; but if it proves that the ammonia is also a product of the decomposition of this intermediate, it must have the formula $\text{C}_2\text{H}_{10}\text{N}_2$, which must also be formed by the association of two molecules of methyl amine. How such association could arise is difficult to visualise; but it is equally difficult to see how an unstable intermediate can arise from the association of ethane and ethylene. The experiments also show that the small quantity of methane and hydrogen which are formed by a process which is rapid only during the first short period, has nothing to do with that which results in the formation of the intermediate which I have discussed. The graphs tend after a time to become approximately parallel, when the only methane and hydrogen produced are formed from the intermediate. The initial formation of hydrogen and methane is probably due to surface action.

This work, which is very difficult, is being continued.

The Ethers.

With the exception of dimethyl ether, the changes involved in the thermal decomposition of these compounds are so very complex, on account of secondary changes, that they do not seem to me to be of great interest. Like all complex changes, when measured by a process which gives the overall rate of a number of reactions, they appear to approach to the form of a unimolecular reaction.

The thermal decomposition of dimethyl ether, measured by observing the rate of change of pressure at constant volume, and applying a correction for the amount of formaldehyde present in the vapour, was found by

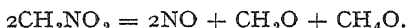
²³ Johnson, *J. Am. Ch. Soc.*, 1916, 1230.

²⁴ Bosanquet, Silcocks, Travers and Wilshire, unpublished.

Hinshelwood and Askey²⁵ to be unimolecular at high pressures, with an energy of activation of 58.5 k. cal. Gay and I,²⁶ for comparable conditions, measuring the rate of formation of methane, found that the κ/t graphs were initially nearly linear, but showed sharp breaks later. The energy of activation for the process was estimated at between 42 and 38 k. cal. While Hinshelwood and Askey found that the process is practically homogeneous, we found that the effect of surface was very marked indeed, the rate depending on the state of the surface of the tube. The results of the experiments on the influence of hydrogen also differ materially. I set down the facts with the comment that it seems generally to be agreed that the behaviour of the ethers is intrinsically different from the compounds with C-C linkages. Hinshelwood and his colleagues incline to the belief that the decomposition process is propagated by short chains,²⁵ and Fletcher²⁶ puts forward evidence that they readily dissociate with formation of free radicals. No explanation which has yet been put forward seems to be satisfactory. I will refer to the reaction of the ethers with nitric oxide later.

The Alkyl Nitrites.

Steacie and Shaw have published a series of papers dealing with the thermal decomposition of the nitrites (Summary of papers I to VIII).²⁷ Their method consisted in heating the vapour in a bulb of pyrex glass, and measuring the change of pressure. Their investigation commenced with the study of methyl nitrite, and from the analysis of the end products they found that carbon monoxide was an important product of the reaction, but they did not observe that nitrous oxide was also formed. From this analysis they applied a correction to the results of their pressure measurements, and came to the conclusion that the thermal decomposition process represented by the equation,



was unimolecular, with an activation energy of 36.4 k. cal. They assumed that a similar process operated in the case of the nitrites of higher radicals, but the whole of their work depends upon the validity of the assumptions which they make in the case of the methyl compound.

Carter and I,²⁸ using the method of detailed analysis determined the rate of formation of nitric oxide, and of carbon monoxide, but we could not devise an analytical method which would enable us to determine the rates of formation of nitrous oxide and of carbon dioxide, which are also products. If the rate of formation of nitric oxide is a measure of the rate of the main reaction, this cannot be represented by a unimolecular formula, as the initial portions of the κ/t graphs bend strongly towards the κ -axis, and show sharp breaks. The slowing down of this process is accompanied by an actual decrease in the concentration of the carbon monoxide, to which I shall refer later.

In the present state of our knowledge, I do not believe that the phenomena associated with the thermal decomposition of such compounds as the nitrites are capable of being interpreted, and if the facts are not fully investigated the results are likely to be more misleading than useful.

General.

With the exception of the case of formaldehyde (p. 1343), we know next to nothing about the simplest reactions, such as are represented by equations 3 and 4. The second is difficult to investigate, as it seems to

²⁵ Hinshelwood and Askey, *Proc. Roy. Soc., A*, 1937, **115**, 215.

²⁶ Fletcher, *J. Am. Ch. Soc.*, 1936, 2129.

²⁷ Steacie and Katz, *J. Chem. Physics*,

²⁸ Carter and Travers, *Proc. Roy. Soc., A*, 1936, **158**, 495.

be catalysed by silica surfaces, and the first, which must have reality unless the basis of organic chemistry is faulty, cannot be investigated in the gas phase by any known method.

From the results obtained in my laboratory, the initial rate of decomposition of all such simple organic compounds as the aldehydes, etc., is self-accelerated. The case of ethane-ethylene-hydrogen mixtures, under certain conditions, is excepted. It may be, of course, that our methods are at fault. However, if our work is correct, it follows that the determination of the order of the reaction from the half-life is not possible, and the results of such attempts are meaningless. This is a logical consequence of the warning uttered by Semenov.¹ It inhibits a common procedure in chemical kinetics. While it is extremely difficult to obtain full information regarding the changes taking place when compounds containing one or two atoms of carbon decompose thermally, the difficulties increase enormously when more complex compounds are dealt with. In the case of a 3-carbon aldehyde, for instance, pyrolysis involves, in the first place, both disruption and condensation. The ethane and ethylene produced by disruption undergo further changes, forming methane, and also condensation product, so that we have to deal with a mixture of compounds containing from one to six carbon atoms. Such complex changes, followed by observing increase in pressure, can generally be represented by formulæ of the unimolecular type; but it remains yet to be proved that the cause of this is other than the complexity of the process.

The Slowing Down of Reactions.

So far I have urged the importance of careful examination of the changes involved during the early stages of a chemical process. It is equally important to study in detail the mechanism of the processes which cause reactions suddenly to slow down, which seems to be a very common phenomenon. In the thermal decomposition of pure ethane, pure ethylene, acetaldehyde, methyl nitrite, etc., the initial stages of thermal decomposition show strong self-acceleration, followed by a sudden slowing down. This slowing down is always accompanied by the speeding up of another process, but it generally happens that the secondary process begins to speed up before the break-point, and slows down again after the break-point is passed. A good illustration of this is the case of the thermal decomposition of pure ethane, when, at the break-point, there is always a drop in the graph representing the rate of formation of hydrogen (Fig. 1). Similarly, in the case of pure ethylene, the hydrogen graph shows (Fig. 4, this vol., p. 243), a sudden rise. The bend in the hydrogen graph forms, in both cases, a loop around the break point.

In the case of methyl nitrite, just before the break in the NO-graph, the CO-graph bends down, carbon monoxide disappearing, probably with the formation of carbon dioxide.²⁸ In the case of acetaldehyde there is a change in the hydrogen concentration at the break-point (Table XII.)¹¹

The case of the slowing down of the normal decomposition of the ethers by nitric oxide, first described by Staveley and Hinshelwood,²⁹ was shown by Gay and myself in the case of dimethyl ether³⁰ to be ac-

²⁸ Staveley and Hinshelwood, *Proc. Roy. Soc., A*, 1936, **154**, 335.

³⁰ Gay and Travers, *Trans. Faraday Soc.*, 1937, **33**, 756.

accompanied by the starting up of a secondary process, involving the disappearance of nitric oxide, and the oxidation of the ether.

The condition necessary for this phenomenon is that the primary centres should reach a high concentration, but whether this can happen without the operation of a chain mechanism may be a question. The phenomenon is only indirect evidence of a chain mechanism, which is a possible cause of the high rate of increase in the concentration of the primary centres. At the same time, some other combination must be present from which secondary centres can arise, in the process of formation of which the primary centres are extinguished. However, it is more facts which are required, and quantitative rather than qualitative investigations.

Conclusion.

I do not think that anyone who is working in this field can feel very satisfied with the position, or confident that we have yet a satisfactory experimental basis on which to build a theoretical structure.

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THE POLYMERISATION OF ETHYLENE AND ACETYLENE PHOTSENSITISED BY ACETONE.

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AND JOSEPH C. JUNGERS, *Aspirant du F.N.R.S., Belgium.*

Received 15th July, 1937.

In addition to the thermal polymerisation of ethylene, various studies dealing with the induced polymerisation by ions,¹ atomic hydrogen,² free radicals from mercury dimethyl³ and azomethane,⁴ by photodecomposition of ammonia,⁵ and with excited mercury,⁶ cadmium,⁷ and sodium⁸ are to be found recorded in the recent literature. The polymerisation induced by ions, atomic hydrogen and excited mercury has been achieved at room temperatures. In the other cases, temperatures in the range 200-300° c. have been employed. The evidence recently accumulated⁹ that the photodecomposition of acetone, from room temperatures upwards, involved a primary production of free radicals offered the possibility to study the influence of alkyl radicals in inducing the polymerisation of ethylene over a similarly wide range of temperatures and to co-ordinate its action with

¹ Mund and Koch, *Bull. Soc. Chim. Belg.*, 1925, **34**, 125, 241; Lind, Bardwell and Perry, *J. Am. Chem. Soc.*, 1926, **48**, 1563.

² Olson and Meyers, *ibid.*, 389; Bates and Taylor, *ibid.*, 1927, **49**, 2438.

³ Taylor and Jones, *ibid.*, 1930, **52**, 1111.

⁴ O. K. Rice and Sickman, *ibid.*, 1935, **57**, 1384.

⁵ Taylor and Emeleus, *ibid.*, 1931, **53**, 562.

⁶ Bates and Taylor, *ibid.*, 1927, **49**, 2438.

⁷ *Ibid.*, 1928, **50**, 771.

⁸ Jungers and Taylor, *J. Chem. Physics*, 1936, **4**, 94.

⁹ Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1934, 1456; Spence and Wild, *ibid.*, 1937, 352.

that of atomic hydrogen and the products of ionisation processes. Thermally, the polymerisation is secured in the temperature range 350-400° c. with an activation energy of 35-42 k.cals.¹⁰ The activation energy of the induced polymerisation is a much lower quantity. The research of Jungers and Taylor which revealed the quenching of excited sodium by ethylene ($\lambda = 5897 \text{ \AA.}$; $E = 48 \text{ k.cals.}$) without measurable polymerisation of ethylene between 150 and 250° c. suggested that the activation energy of the thermal process is required to effect the breaking of a carbon-hydrogen linkage producing a free radical, the polymerisation thus induced being a process of much lower activation energy. The following results on the induced polymerisation of ethylene by the radicals from the photodecomposition of acetone from room temperatures up to 250° c. support this point of view. They also reveal the complexity of the acetone photodecomposition process, in agreement with the recent findings of Spence and Wild.

In the case of acetylene it is known that polymerisation with the formation of cuprene and other polymers can be produced by alpha particles,¹ cathode rays,¹¹ excited mercury⁶ and by photochemical action.¹² It has not been shown unambiguously, that atomic hydrogen produces polymerisation. Our experiments indicate definitely that the free radicals from acetone photodecomposition produce polymerisation of the gas.

Experimental Procedure.

Various mixtures of acetone vapour and ethylene or acetylene could be introduced from reservoirs of the carefully purified materials into a cylindrical quartz reaction vessel, 19 cm. long and 2.3 cm. in diameter, mounted vertically. This vessel could be enclosed in an aluminium block electric furnace giving an even temperature distribution, illumination entering through a quartz tube placed snugly in a cut-away section of the furnace, the length of the reaction vessel. Ultra-violet light, from a hot mercury arc of the Heraeus type, operated vertically (arc length = 12 cm.), entered the reaction vessel through a cylindrical quartz vessel containing a continuously renewed stream of 25 per cent. acetic acid to reduce the intensity of the short wave-length ultraviolet light capable of producing the photochemical polymerisation of ethylene. The interposition of the two quartz tubes between light source and reaction vessel resulted in a separation of these two by a distance of 8 cm., in all the experiments above room temperature. At this last temperature the quartz-acetic acid filter alone was interposed, and the arc source was approximately 4.5 cm. from the reaction vessel.

The reaction vessel was suitably connected to an oil pump-mercury vapour pump high vacuum source, to the reservoirs of reaction materials, to a mercury manometer and to a tube containing copper oxide, which could be electrically heated. With this latter, the fraction of gases non-condensable in liquid air, resulting from an experiment, could be accurately analysed for carbon monoxide and methane.

Manometrically, the pressure changes occurring during illumination were recorded, and also the final pressures at room temperatures and after the condensable materials had been removed by liquid air. From these data, the course of the photo-decomposition and the consequent polymerisation could be deduced.

Experiments have been made at 25°, 80°, 140° and 250° c. As will

¹⁰ Pease, *J. Am. Chem. Soc.*, 1931, **53**, 613; Storch, *ibid.*, 1934, **56**, 374.

¹¹ McLennan, Perrin and Ireton, *Proc. Roy. Soc., A*, 1929, **125**, 246.

¹² Lind and Livingston, *J. Am. Chem. Soc.*, 1932, **54**, 94.

be shown, those at ordinary temperatures are complex, due to the complexity of the acetone decomposition. At 80° and upwards the processes become much simpler in nature.

Experimental Results.

The effects produced by variation of (a) acetone concentration, (b) ethylene concentration, and (c) intensity of illumination at the several temperatures have been systematically studied and are recorded in the following paragraphs:—

(a) **Variation of Acetone Concentration.**—The effects of acetone concentration between the limits of 0.67 and 15.6 cm. have been studied at the four temperatures with an ethylene concentration maintained approximately constant at ~ 15 cm. pressure. The experimental data are recorded in Table I.a. In all of the experiments, save one (11), the increase in gas pressure which would result from photo-decomposition of the acetone has been converted into a pressure decrease by the simultaneous polymerisation of the ethylene. In Experiment 11 also, the change in pressure was first negative, then positive and always small throughout the experiment even though 15 cm. of acetone were decomposed. It is evident that, in this case, amounts of ethylene equivalent approximately to the acetone decomposed must have been polymerised. The efficiency of the photo-decomposition in terms of ethylene polymerised is shown in the column headed M/N . This gives the ratio of the sum $(\Delta P + CO)$ to CO , that is to say, the total pressure decrease due to ethylene polymerisation as a function of acetone decomposed measured by carbon monoxide formation. Such a calculation assumes that photo-decomposition yields equivalent volumes of ethane and carbon monoxide. The gas analyses show that such is not quantitatively true, especially at the highest temperature, where methane formation becomes quite important. The effect of introducing such corrections for methane would be still further to increase the value of M/N .

The conclusions to be drawn from such data are not immediately obvious but careful examination shows that the following conclusions can readily be made. The polymerisation efficiency increases with increasing temperature. It increases also with decreasing acetone concentration. In the data at the lower temperatures, 20° and 80° c., the efficiency appears at first to decrease with decreasing acetone concentration. This is to be ascribed to the effect of self-polymerisation of the acetone on the calculated polymerisation efficiency. This is to be seen from Experiment 9 in Table I. (b), with acetone alone, where the increase in pressure due to photo-decomposition is *less* than the carbon monoxide produced, which can only mean some polymerisation of acetone. When corrections are introduced for this side-reaction the polymerisation yield, even at the lower temperatures, increases steadily with decreasing acetone concentration. Experiment 17 at 250° C., which appears to be out of line with these conclusions, shows a low M/N value because of the prolonged nature of the experiment in comparison with the others, as seen from the large yield of carbon monoxide (*cf.* expt. 20). The initial yield in this experiment was also in the neighbourhood of 3.

At the highest acetone concentrations (~ 15 cm.) the M/N values appear to decrease with increasing temperature from 25° to 140° c. We ascribe this to complexities in the acetone decomposition at lower temperatures recently exhibited by Spence and Wild. They have shown that, at ordinary temperatures, the acetyl radicals, resulting from decomposition, form diacetyl. We suggest that, in presence of free methyl radicals, this diacetyl may be decomposed with regeneration of acetone. Such regeneration would account in part for the very low quantum yields of acetone decomposition found at ordinary temperatures. Such regeneration of

TABLE I.

Experiment No.	Acetone P cm.	Ethylene P cm.	ΔP .	Carbon Monoxide P cm.	CH ₄ /CO (× 100).	M/N.	Time in Hours.
A. Influence of Acetone Concentration.							
25° C.							
4	15.46	14.84	— 1.43	3.25	5.7	1.44	—
6	8.15	16.69	— 0.79	2.64	8.4	1.31	17.75
7	4.01	15.46	— 0.47	1.78	10.5	1.26	—
3	1.78	18.0	— 0.61	0.50	14	2.21	—
80° C.							
22	15.58	16.24	— 0.77	2.63	6.6	1.29	1.0
21	8.38	16.22	— 0.54	3.57	6.5	1.15	2.5
140° C.							
11	15.27	15.05	+ 0.53	15.1	11.5	0.97	15.1
12	8.32	14.88	— 1.76	4.18	8.6	1.38	1.16
13	2.59	15.68	— 5.23	2.3	7.1	3.28	13.5
14	1.00	14.58	— 4.58	0.94	6.0	5.9	13.0
15	8.9	14.91	— 8.39	3.64	20	3.3	14.5
250° C.							
23	15.32	16.06	— 5.83	2.44	26.4	3.4	0.11
17	8.9	14.8	— 6.85	7.15	39	1.95	0.9
20	8.57	14.61	— 6.02	2.95	22	3.04	0.25
24	1.27	14.83	— 6.75	1.2	—	6.6	2.5
27	0.67	15.28	— 4.56	0.66	—	7.8	2.5
B. Influence of Ethylene Concentration.							
25° C.							
5	15.57	0	+ 3.48	5.50	4.4	0.37	11.0
	15.5	5.43	+ 1.13	4.6	5.0	1.02	16.0
4	15.46	14.84	— 1.43	3.25	5.7	1.44	—
8	16.51	34.24	— 2.45	3.12	7.7	1.78	12.9
250° C.							
28	1.29	7.46	— 3.58	1.29	—	3.77	2.5
24	1.27	14.83	— 6.75	1.27	—	6.3	2.5
30	1.45	24.48	— 9.57	1.32	—	8.2	1.25
25	1.26	30.69	— 12.80	1.26	—	11.1	2.5
29	1.38	53.3	— 15.02	1.38	—	11.9	2.5
C. Influence of Light Intensity.							
140° C.							
12	8.32	14.88	— 1.76	4.18	8.6	1.42	1.16
15	8.65	14.91	— 8.39	3.64	20.0	3.4	14.5
250° C.							
18	8.12	—	+ 2.26	2.54	73	—	0.9
19	8.26	—	+ 2.92	2.98	42	—	15.0

acetone would have the effect of increasing its efficiency for ethylene polymerisation in the manner which we have found.

Attention should also be directed to the divergencies between low and high temperature measurements as revealed by the methane formation.

We confirm the result of Spence and Wild that, at the low temperatures, decrease of light intensity leads to increase of methane formation, other variables being constant. Our data indicate that, at these temperatures also, in presence of ethylene, low free radical concentration favours methane formation. In our experiments at low temperature, with ethylene present, we do not

find that the methane increases with acetone pressure, contrary to the results of Spence and Wild with acetone alone. With ethylene present, however, there is, obviously, a competition between at least two substances for free methyl radicals and our methane may result from the polymerisation processes. At our highest temperatures, 140° and 250° C., the methane formation is much more pronounced, and, in this case, parallels the acetone pressure; but it is also least pronounced where the polymerisation yield is greatest, so that it is not possible to say which is the determining factor.

Fig. 1 shows graphically the influence of acetone concentration on the velocity of polymerisation at constant ethylene pressure and 250° C.

(b) Variation of Ethylene Concentration.—The experiments to determine the influence of ethylene concentration are presented in Table I.b. Two temperatures 25° and 250° C. have been chosen. At the low

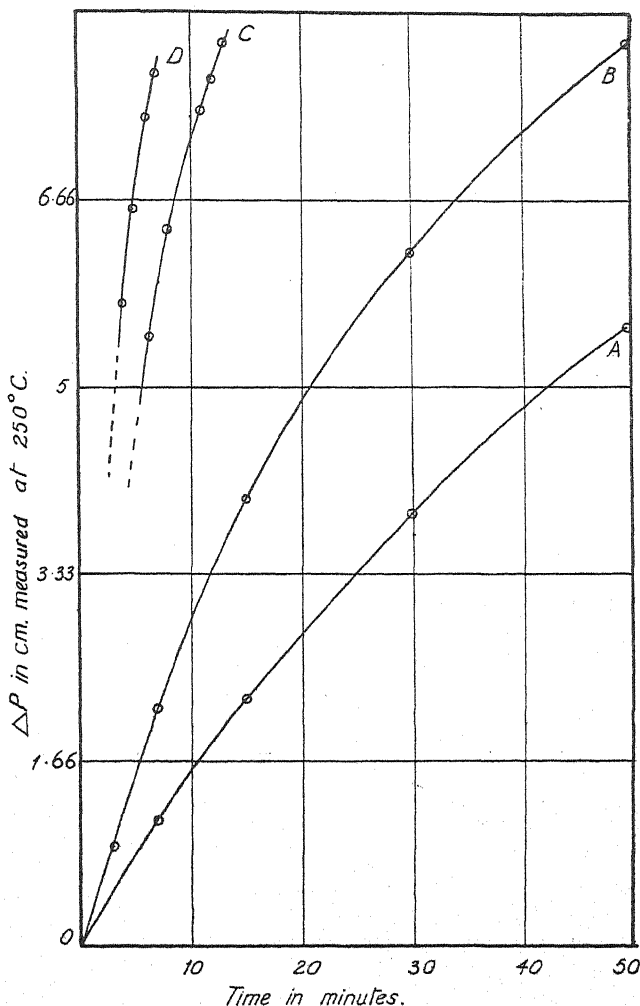


FIG. 1.—Velocity of polymerisation with varying acetone pressure.

- A. 0.7 cm. acetone; 15 cm. ethylene.
 B. 1.3 cm. " ; 15 cm. "
 C. 8.6 cm. " ; 15 " "
 D. 15.3 cm. " ; 16 " "

temperature it was necessary, owing to the low quantum yield of acetone decomposition, to employ a high acetone concentration (~ 15 cm.). At 250°C . the measurements could readily be performed with an acetone concentration of 1-15 cm. In each case the polymerisation efficiency increases with increasing concentration of ethylene, and, in this set of

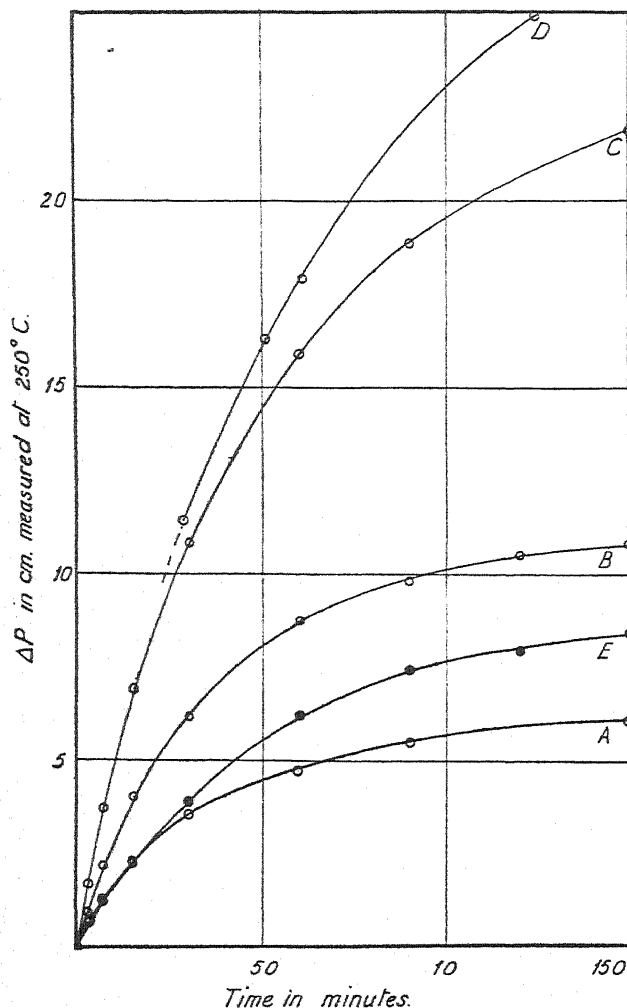


Fig. 2.—Induced polymerisation at 250°C ., and varying pressure of ethylene.

- A. 1.3 cm. acetone; 7.5 cm. ethylene.
 B. " " ; 15 " "
 C. " " ; 30 " "
 D. " " ; 50 " "
 E. 0.7 cm. " ; 15 " "

cm. ethylene. From the initial slopes of the curve — $\Delta P/\Delta t$ it is apparent that, within the interval of ethylene pressure, 7.5-30 cm., the kinetics are given by an expression of the form

$$-\Delta P/\Delta t = k[\text{CH}_3][\text{C}_2\text{H}_4]$$

data, as in the case of the preceding section, the quantum yield of polymerisation increases with increase of temperature.

The experiments at 250°C . are the most convenient with which to obtain a quantitative interpretation of the kinetics of the process. For, with the minor concentrations of acetone involved, the decrease in pressure with time is an approximate measure of the rate of polymerisation. We present the actual data thus secured in Fig. 2 for mixtures of 1.3 cm. of acetone with 7.5, 15, 30 and 50 cm. of ethylene and, for comparison, with the first of these mixtures, a curve with 0.7 cm. acetone and 15

where the methyl radical concentration is determined by the product of light intensity and acetone pressure, $I_0[\text{CH}_3\text{COCH}_3]$.

For total pressures below 6 cm., O. K. Rice and Sickman found a proportionality to the three-halves power of the ethylene pressure in the polymerisation induced at 300° by decomposition of azomethane. In such a low pressure range the wall effect must play a much more important rôle in the breaking of the reaction chains, the effect of which would be to increase the order found with respect to ethylene. It is to such a factor that we ascribe the divergence between our result and theirs. At our highest pressure, 53.3 cm. of ethylene, we have evidence that the rate of polymerisation is becoming independent of the pressure. This is readily understood if the polymerised product is removed from the heated zone of reaction as a condensable liquid, a phenomenon which we always observed.

(c) **Variation of Light Intensity.**—Since low acetone concentrations favour increasing efficiency of polymerisation it would be anticipated that decreasing light intensity, producing a lower stationary state concentration of radicals, would also lead to higher polymerisation efficiency. This we have demonstrated in two experiments at 140° C. recorded in Table I.(c). From the times required to produce a given pressure of carbon monoxide a variation in light intensity in the ratio of 15 : 1 was deduced. This caused a change in polymerisation efficiency from $M/N = 1.42$ at the higher intensity to 3.4 at the lower. In agreement with Spence and Wild, we find also, in these experiments, an increase of methane production from 8.6 to 20 per cent. with the same decrease in light intensity. With acetone alone at 250° C., as the data in Table I. (c) also show, a four-fold decrease in light intensity causes a change in methane production from 42 to 73 per cent.

(d) **Acetylene Polymerisation.**—The data in Table II. show that the photo-sensitised polymerisation of acetylene may be secured at 25° C. The number of molecules polymerised per unit decomposition of acetone increases with increasing acetylene pressure, and with increasing temperature. The influence of the several variables is much less pronounced than in the case of ethylene. Our yields per unit of acetone decomposed are less than those secured by alpha particles, excited mercury and photo-chemical decomposition. A viscous polymer was deposited upon the walls of the reaction vessel in amounts too small for further examination.

TABLE II.—POLYMERISATION OF ACETYLENE.

Experiment No.	Acetone <i>P</i> cm.	Acetylene <i>P</i> cm.	ΔP .	Carbon Monoxide <i>P</i> cm.	<i>M/N</i> .	Time in Hours.	<i>T</i> ° C.
31	1.63	14.37	— 6.12	1.5	5	2.5	250
33	14.46	19.42	— 5.42	1.32	5.1	0.11	250
34	13.18	8.90	— 3.50	1.48	3.35	0.11	250
36	12.28	15.14	— 3.84	2.18	2.75	14.0	20
37	15.93	16.67	— 5.62	2.58	3.18	0.75	140
32	—	17.23	— 1.95	—	—	0.5	250
35	—	12.0	— 0.57	—	—	35.0	20

General Discussion.

The occurrence of ethylene polymerisation in presence of methyl radicals at room temperature and the relatively small influence of temperature on the polymerisation process in such systems lead at once to several interesting conclusions. They indicate that the activation energies obtained in the processes of thermal polymerisation (35-42 k.cals.), are not determined by the polymerisation process itself but

characterise the activation process necessary to start the polymerisation. It may be suggested that this activation involves the formation of a free radical. Also, although ethylene quenches excited sodium, it is not polymerised below 250° c. in presence of these excited atoms, in contrast to the rapid polymerisations here recorded. We thus conclude that the quenching process with sodium does not result in the formation of free radicals. With mercury and cadmium, on the contrary, it would appear that quenching leads to free radical formation, and hence to the polymerisation observed.

The highest ratios of ethylene molecules polymerised to acetone molecules decomposed which are observed in the experiments at 250° c., are similar in magnitude to those observed in the polymerisation induced by thermal decomposition of metal alkyls,³ and these in their turn are similar to those obtained with alpha particles¹ at room temperature. The yield in the case of acetylene at room temperature is somewhat less than with alpha particles but the influence of temperature is similar. Attention should be drawn to the influence of radical concentration on polymerisation. Low radical concentration favours increased polymerisation yield. With low acetone concentrations, at 250° c., the initial rate of polymerisation reached 11 molecules ethylene polymerised to unit methyl radical introduced. This assumes, moreover, that every acetone molecule decomposing yields two methyl radicals, which represents the upper limit possible.

Summary.

1. The induced polymerisation of ethylene and of acetylene can be secured at room temperatures and upwards by photodecomposition of admixed acetone.
2. The polymerisation is attributed to the action of radicals produced in the photo-decomposition process.
3. The polymerisation yield increases with increasing temperature, decreasing concentration of acetone and decreasing light intensity.
4. At low ethylene concentrations polymerisation is proportional to the ethylene concentration, but becomes independent of this above 30 cm. pressure.
5. The data obtained suggest that free radicals play a rôle in other methods of securing polymerisation.

*Laboratoire de la Chaire Francqui, 1937.
University of Louvain,
Belgium.*

REVIEWS OF BOOKS.

The Mechanism of Contact Catalysis. By R. H. GRIFFITH, Oxford University Press, Milford. 15s. net.

During the last few years the literature on the subject of heterogeneous catalysis has increased in a way with which nobody but a specialist can keep pace. The present volume is therefore to be welcomed, as it provides a useful guide book to this intricate maze of facts and theories. If it does not illuminate the subject with any important synthesis, the book certainly gives an accurate, up-to-date and well-balanced account

of most of the important work on catalytic reactions at surfaces which has appeared during the past decade.

After a useful chapter on experimental methods it deals with the phenomena of adsorption, then with promoters, with poisoning, with various aspects of the catalytic surface, and with the mechanism of catalysis. The logical structure of the book is not very clear, though, accepting the author's arrangement, his treatment is usually clear and his comments sound. Dr. Griffith has worked on catalytic reactions in the laboratories of the Gas Light and Coke Company, and the book contains an interesting account of work done in these laboratories on mixed catalysts and promoter action. It is a pity that slightly unscientific methods of representation are sometimes employed such as "yield"-temperature diagrams—which give only a rough indication of the change of the reaction velocity. But this does not obscure the practical significance of the results.

The book will be found of great service by industrial chemists and, by those whose interest in the matter is more general, a useful summary of information.

Intermediate Chemistry. By T. M. LOWRY and A. C. CAVELL. Pp. xvi + 876. London: Macmillan & Co. Ltd., 1936. Price 12s. 6d.

The book aims at providing in a single volume a complete theoretical and practical text-book for the Intermediate and Higher School Certificate Examinations. It is divided into separate sections on General and Theoretical Chemistry (pp. 1-61), Inorganic Chemistry (pp. 63-375), Qualitative and Quantitative Analysis (pp. 377-451), Physical Chemistry (pp. 453-650), and Organic Chemistry (pp. 651-801). At the end is a selection of examination questions. A special feature is made of the large number of experiments, listed at the beginning of the book. The general treatment is clear and the standard is more than adequate for the examinations named, going well beyond the requirements in the sections on atomic structure, physical chemistry and organic chemistry, so that scholarship students will find the book useful. A good feature in an elementary book is the tabulation of the properties of groups of elements. Very few errors have been detected, the worst being the inaccurate account of the Joule-Thomson effect on pp. 479-480. The capacity of Lowry for making difficult subjects easy is well illustrated in the present book, which continues the high standard of those published during his life.

J. R. P.

Physical Chemistry. By F. H. MACDOUGALL. 1st Edition. (New York. The MacMillan Company, 1936. Pp. vii and 721. Price 17s.)

This is a textbook of elementary physical chemistry in the best traditional vein. According to the preface, it "offers to the student who has had a year's course in physics and who has mastered the fundamental operations of the differential and integral calculus an opportunity to acquire a sound and working knowledge of physical chemistry." We venture to think that the author has attained his objective with supreme ease. There is, moreover, much here that will be welcomed by many

others who have long passed their first year of physics. There is throughout a happy blend of sound thermodynamical treatment with well-documented experimental facts. The atomic processes are carefully outlined, and the book throughout is written with admirable clarity.

One would feel happier if somewhat greater prominence were given to the Quantum Theory. For example, on page 156 we are given the familiar expression of Planck for the average energy of a quantised oscillator. In view of the fundamental importance of Planck's method, and of the simplicity of the algebraic steps, it is a pity that the brief derivation has not been given. Its absence may cause the newcomer to physical chemistry to invest the quantum theory with a mystery which it does not deserve. However, this is a minor point which would not have been commented upon were it not for the uniform reliability and high standard of the work as a whole.

Professor MacDougall is to be warmly congratulated on writing a book which should find a wide circulation in this country. The format is worthy of the MacMillan Company, and at the published price the book is very good value.

E. A. M. H.

CORRIGENDA.

After going to press the following amplification of page 1336, lines 5 to 10, was received from the authors:—

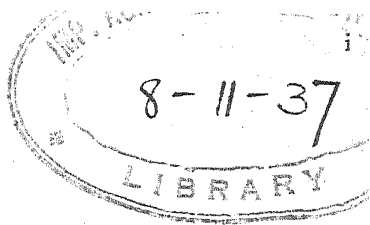
At any given wavelength, the total absorption is made up of contributions from molecules in different vibrational levels of the ground state. If ϵ_v is the absorption coefficient at this wavelength for molecules in the level whose vibrational quantum number is v , and if N_v is the fraction of the molecules that occupy that level, then for the given wavelength—

$$\epsilon = N_0\epsilon_0 + N_1\epsilon_1 + N_2\epsilon_2 + \dots$$

Values of ϵ_0 and ϵ_1 can be found from the data in Table I. by the method of temperature analysis that has been described by Gibson and Bayliss.⁴ They showed that if E_v is the spectroscopically determined energy of the state v , one can calculate for each experimental temperature the (partition) function $S_T = \sum_v \exp[-(E_v - E_0)/kT]$. If the values of ϵ , at one wavelength but at the different temperatures, are each multiplied by the appropriate value of S_T , then one can put—

$$\epsilon S_T = \epsilon_0 + \epsilon_1 x + \epsilon_2 x^2 + \dots$$

where $x = \exp(-hc\omega/kT)$, ω being a mean value for the separation between successive low vibrational levels of the ground state. For chlorine, we put $\omega = 551 \text{ cm}^{-1}$. At each wavelength, ϵS_T for each temperature is plotted against the appropriate x , and ϵ_0 and ϵ_1 for that wavelength are given by the ordinate and gradient respectively that are found on extrapolating the curve to the point $x = 0$.



The Faraday Society.

MINUTES OF THE THIRTY-FIRST ANNUAL GENERAL MEETING.

*Held on Tuesday, 14 September, 1937, at 9.45 a.m.
in the Chemistry Department of the University of Manchester.*

PROFESSOR MORRIS W. TRAVERS (PRESIDENT) IN THE CHAIR.

1. The Minutes of the Thirtieth Annual General Meeting were taken as read.

2. The Annual Report and Statement of Accounts for the year 1936 were submitted by the Secretary on behalf of the Honorary Treasurer and, no questions from the members being forthcoming, were adopted. In moving the adoption, the Secretary presented the apologies of the Honorary Treasurer who was prevented from being present, and read the Honorary Treasurer's statement as follows :—

I am glad, in presenting and moving the adoption of the accounts for the year 1936, to be able to report a credit balance for the year amounting to £238 2s. 5d. This improvement in the Society's affairs, to the tune of no less than £549 13s. 4d. from the debit balance of £311 9s. 11d. in 1935, was due mainly to economy in printing and to increased revenue from subscriptions and sales, details of which will be found in the report of the Council, which has been before the members for some weeks.

You will notice that the form in which the accounts are set out this year, have been modified by the elimination of the sub-division of the Income and Expenditure Account and by incorporating the various items in the main Income and Expenditure Account and the Balance Sheet. This alteration makes the accounts more easily understandable.

I should like to say a few words with regard to economy in printing. During 1936 we published 218 papers as compared with 196 in 1935; if we neglect the half-tone plates, these additional 22 papers occupied only 11 pages more than the 196 papers in 1935. Moreover, the cost of printing them was £207 9s. 9d. less, despite the fact that owing to the increased membership and increased sales we had to print larger editions.

In my statement last year I referred to some of the steps the Council were taking to reduce the costs of printing. Those steps were only effective for part of the year 1936; the first 412 pages of Volume XXXII were devoted to the report of the meeting held in September 1935, and under our new arrangements such reports will be reduced to a size of about 250 pages. We have published two reports in this smaller size, namely,

"Disperse Systems in Gases" (260 pages) and the Edinburgh Discussion on "The Liquid State" (282 pages). I believe that members will agree with me that these reports have gained in clarity and conciseness, and I am glad to say that we are able to sell them at a lower price so that they serve to disseminate even more widely than before the good work which the Society is seeking to do. Our revenue from the sales of these Reports continues to be satisfactory.

The credit balance for the year, as you will have noted, has been deducted from the "Debit Balance brought forward" appearing in the Balance Sheet, which reduces this item to £168 1s. 10d.—I am looking forward to wiping out this debit balance next year and thus being in a position to present you with a clean healthy balance sheet.

Unfortunately, owing to increasing cost for overheads in the printing trade, coupled with the still rising prices for paper, we are still having some anxiety in the already difficult task of keeping our expenditure within the bounds of our income. However, there is also a bright feature—I am sure you will agree with me that the increase in our membership last year was highly satisfactory and reflects great credit on the members and also our esteemed Secretary for the efforts made in this direction. While we are able to continue to replenish our yearly losses and to increase our membership year by year, we need have no undue anxiety as regards the financial position nor any question of limiting the many useful activities of the Society.

3. The President declared the Council for the year 1937-38 to be elected in accordance with the notice convening the meeting. The Council so elected was :—

President.

PROF. M. W. TRAVERS, D.Sc., F.R.S.

Vice-Presidents who have held the Office of President.

SIR ROBERT ROBERTSON, K.B.E., D.Sc., F.R.S.

PROF. F. G. DONNAN, C.B.E., Ph.D., F.R.S.

PROF. C. H. DESCH, D.Sc., F.R.S.

SIR ROBERT L. MOND, LL.D.

PROF. N. V. SIDGWICK, Sc.D., D.Sc., F.R.S.

Vice-Presidents.

U. R. EVANS, Sc.D.

PROF. W. C. M. LEWIS, D.Sc., F.R.S.

PROF. A. FERGUSON, D.Sc.

PROF. J. R. PARTINGTON, M.B.E., D.Sc.

PROF. C. N. HINSHELWOOD, Sc.D.,
F.R.S.

PROF. E. K. RIDEAL, M.B.E., D.Sc.,
F.R.S.

PROF. J. C. PHILIP, D.Sc., C.B.E., F.R.S.

Honorary Treasurer.

EMILE S. MOND.

Council.

J. D. BERNAL, M.A.

PROF. J. KENDALL, D.Sc., F.R.S.

H. J. EMELÉUS, D.Sc.

A. McKEOWN, D.Sc.

PROF. W. E. GARNER, D.Sc.

PROF. M. POLANYI, Ph.D., M.D.

S. GLASSTONE, Ph.D., D.Sc.

D. W. G. STYLE, Ph.D.

C. F. GOODEVE, D.Sc.

PROF. S. SUDGEN, D.Sc., F.R.S.

4. On the motion of the President a vote of thanks was accorded to the retiring Vice-President and Ordinary Members of Council, and the thanks of the Society were accorded to the Honorary Treasurer.

This concluded the business of the meeting.

NOTE ON CO-ORDINATION NUMBERS EIGHT.

By W. G. PENNEY AND J. S. ANDERSON.

Received 10th June, 1937.

According to the empirical "covalency rule," the maximum covalency of elements in the first short period of the periodic table is four, and of elements in the second short period or the first long period (*i.e.*, from Na to Br) is six. Elements of higher atomic number are considered to have maximum co-ordination number eight.

Complex ions and molecules involving an apparent group of eight atoms around a central atom are rare, although groups of four and six are common. An examination of the compounds which have been considered to come within the first-mentioned category shows that the range of eight-co-ordinated compounds is limited to a very few elements.

Thus, zirconium, thorium and cerium form double sulphates and oxalates of the general type $K_4[M(SO_4)_4]$. Whether such a formula truly represents their structure is somewhat doubtful, since in the case of thorium, at least, there may also be obtained compounds formulated¹ as $K_6[Th(SO_4)_5] \cdot 3H_2O$ and $K_8[Th(SO_4)_6] \cdot 2H_2O$. There is no evidence that any of these are other than lattice compounds of the general type $M(SO_4)_2 \cdot nK_2SO_4$, where $n = 2, 3$ or 4 . On the other hand, as will be seen from the following discussion, the formation of eight-co-ordinated compounds is possible in the cases of Zr, Ce and Th, so that the complex $[M(SO_4)_4]^{4-}$ may very well exist as a structural unit.

The double fluorides Na_3TaF_8 , Li_4ZrF_8 , $K_3H(MF_8)$, where $M = Ta$, Sn or Pt , undoubtedly are not examples of co-ordination number eight, but are lattice compounds $NaTaF_6 \cdot 2NaF$, $K_2TaF_6 \cdot KHF_2$, etc., just as has been shown to be the case² with the compounds of supposed co-ordination number 7 and 5. In the same way, the octohydrated salts, mostly of divalent metals, may be eliminated from consideration, since such salts are formed indiscriminately by magnesium, calcium and nickel—for which the maximum covalency is six, and which are known invariably to form octohedral hexahydrated ions—as well as by the heavier metals barium and thorium, for which eight-co-ordination is possible. It is, in any case, doubtful how far hydrated ions should be regarded as formed by true covalencies.

Certain compounds of osmium and ruthenium, zirconium and hafnium, molybdenum and tungsten, remain for consideration. The typical compound is clearly $OMoF_8$. With it must be ranked $OMoO_4$ and RuO_4 since doubly linked oxygen fills two co-ordination positions. Zirconium acetylacetonate, and the analogous compounds of cerium and hafnium, are unambiguously eight-co-ordinated.

Amongst complex salts, $K_4Mo(CN)_8$, $K_2Mo(CN)_8$, and $K_4W(CN)_8$ demand attention. That the first of these, in particular, is a true

¹ See, for example, Weinland, *Einführung in die Chemie der Komplexverbindungen*, Stuttgart, 1923, pp. 223, 297 *et seq.*

² For example, $(NH_4)_2ZrF_7$; Hassel and Mark, *Z. Physik*, 1924, 27, 89.

complex, and not, for example, a lattice compound of $K_2Mo(CN)_6$ with KCN is shown by the careful work of Bcuknell and Wardlaw.³

To sum up the experimental evidence, we may therefore say that at most only eight elements Zr, Mo, Ru, Ce, Hf, W, Os, and Th exhibit co-ordination number eight.

The reason for the rarity of co-ordination number eight is understandable. Thus, as Pauling⁴ has shown, four atoms grouped tetrahedrally about a central atom require *s* and *p* orbitals available on the central atom. When, in addition, *d* orbitals are available, the four attached atoms may pass into a square configuration, or a complex may be formed with six atoms grouped octahedrally. A complex with eight attached atoms, however, as Van Vleck⁵ has recently shown, is unlikely to be stable unless *s*, *p*, *d* and *f* orbitals are available on the central atom. Since the mere presence of electrons on the central atom in these four types of orbital will not be a sufficient condition to give a co-ordination number eight, and atoms with *f* electrons do not occur in the first half of the periodic table, it is clear that not many elements should be able to form an eight co-ordinated complex. Lennard-Jones,⁶ before the appearance of Van Vleck's paper, had indeed suggested that only very heavy elements could do so, partly because a large central atom is required in order that eight atoms can be packed around it, and partly because only very heavy elements could have atomic orbitals with sufficient nodes to fit in with the symmetry properties of eight attached atoms.

Perhaps it is worth pointing out that, in spite of its plausibility, the first of these reasons cannot in any case apply. A clear distinction must be drawn between "co-ordination" as used in the strict chemical sense, and as used in crystallography. In the latter sense, the co-ordination number is governed by the radius ratio of the atoms concerned. Where chemical combination occurs, however, it is an invariable rule that the stable co-ordination number increases with increase in positive valency. Thus the platinous ion (radius 0.93 Å.) has the co-ordination number four—e.g., K_2PtCl_4 , $[Pt(NH_3)_4]Cl_2$; while the platinum ion (radius 0.69 Å.) has the co-ordination number six—e.g., K_2PtCl_6 , $[Pt(NH_3)_6]Cl_4$.

Most of the eight elements showing co-ordination number eight are heavy elements, and thus fit in with the considerations sketched above. More surprising are Zr and Mo, of atomic numbers 40 and 42 respectively. To account for the valency properties of these two elements one must make the very reasonable assumption that, although it is necessary to go as far as Ce, atomic number 58, in the periodic table before reaching a neutral atom with any *f*-electrons, yet in a complex system such as $[Mo(CN)_8]^{4-}$, where there are several more electrons than there would be if the system were electrically neutral, the 4*f* orbit is comparable in stability with the other orbits of the 4-shell.

Orbitals of the Eight Co-ordinated Complex.

For simplicity, assume that each of the attached atoms is equivalent. Then Van Vleck⁵ writes a molecular orbital of the complex in the form

$$\psi = p\psi(C) + q \sum_i a_i \psi_i, \quad \dots \quad (I)$$

³ *J. Chem. Soc.*, 1927, 2981.

⁴ *J. Am. Chem. Soc.*, 1931, **53**, 1367.

⁵ *J. Chem. Physics*, 1935, **3**, 803.

⁶ *J. Soc. Chem. Ind.*, 1934, **53**, 249.

where $\psi(C)$ is an atomic orbital of the central atom conforming to the symmetry of the system as a whole, ψ_i is the atomic orbital of the attached atom i , a_i is either $+1$ or -1 according to the value of i and the particular orbital under consideration, and p and q are constants whose relative magnitudes measure the ionic character of the complex. The only orbitals of the central atom which will give bonding are those having symmetry properties which can be matched by an expression of the form $\sum_i a_i \psi_i$. Van Vleck finds that when the eight attached atoms

are arranged at the cube corners around the central atom, orbitals of the symmetry types A_{1g} , T_{1u} , T_{2g} and A_{2u} , in Mulliken's notation,⁷ can be constructed as linear combinations of orbitals of attached atoms. All of these can be matched by orbitals of the central atom, provided s , p , d and f orbitals are available.

Let us suppose that the central atom has the $1, 2 \dots, (n-1)$ shells complete, and has some electrons in the n and $(n+1)$ shells. The Table I. shows which orbitals of the central atom are to be associated with the orbitals of the attached atoms.

The last column shows the electron capacity of the molecular orbitals of the complex which result from an application of equation (1). Thus, for example, from the attached orbital

TABLE I.

Symmetry Type of Attached Orbital.	Associated Orbitals of Central Atom.	Electron Capacity of Bonding Orbitals.
A_{1g}	$A_{1g}(ns), A_{1g}(\overline{n+1s})$	4
T_{1u}	$T_{1u}(np), T_{1u}(\overline{n+1p})$	12
T_{2g}	$T_{2g}(nd)$	6
A_{2u}	$A_{2u}(nf)$	2

of symmetry type A_{1g} , and the orbitals $A_{1g}(ns)$ and $A_{1g}(\overline{n+1s})$ of the central atom, three molecular orbitals of the complex may be constructed. Two of these are strongly bonding, and each takes up two electrons. Accordingly, the capacity is 4. There are also two strongly bonding orbitals of the T_{1u} type. Since T orbitals are triply degenerate, and therefore capable of absorbing six electrons, the bonding T_{1u} orbitals accommodate in all 12 electrons. The bonding T_{2g} orbital takes up 6 electrons, and the bonding A_{2u} orbital, two.

The results summarised in Table I. may also be expressed in terms of the electron-pair theory of valency. In short, according to the pair theory, the configuration of the central atom is $(ns)^2(np)^6(nd)^3(nf)(\overline{n+1s})(\overline{n+1p})^3$. Eight equivalent directed wave functions may be constructed from the eight atomic orbitals $(nd)^3(nf)(\overline{n+1s})(\overline{n+1p})^3$ of the central atom, and these are to be paired off, each with the single valence electron of an attached atom.

From Table I. it is seen that 24 electrons can be absorbed into bonding orbitals in an eight-co-ordinated complex. Six of the eight elements which actually exhibit co-ordination number eight bear this out; they all form stable groups of 24 electrons. (In counting the number of electrons controlling the valency properties F , for example, counts as contributing one, because F has only one valency electron.) The two

exceptions are Mo and W. Examples are $[\text{Mo}(\text{CN})_8]^{3-}$, which has a group of 25 valency electrons, and $[\text{Mo}(\text{CN})_8]^{4-}$ and $[\text{W}(\text{CN})_8]^{4-}$ which have 26 valency electrons. No example is known where more than 26 electrons are involved. We must now interpret these facts.

The Complex with 26 Valency Electrons.

To account for the existence of ions with stable groups of 25 and 26 valency electrons, a further orbital, comparable in stability with those of Table I., must be found. There are only three possibilities. One is the third A_{1g} orbital of Table I.; this can at best be only weakly bonding, and may very well be slightly anti-bonding (see the following section). The other two are orbitals of the central atom not matchable by combinations of orbitals of attached atoms, namely $E_g(nd)$ and $T_{2u}(nf)$. Clearly $T_{2u}(nf)$ is not as stable as $E_g(nd)$. The issue has thus been reduced to deciding which is the more stable of A_{1g} and E_g . Unfortunately, it is impossible to proceed any further on purely theoretical grounds. An appeal to experimental observation, however, definitely settles the matter.

Let us suppose that $E_g(nd)$ is more stable than the particular A_{1g} under discussion. Then, as we have seen, a stable closed group of 24 electrons can be absorbed in the orbitals described by Table I. When a further electron is added, it passes into the $E_g(nd)$ orbital, and the system is paramagnetic, because the total number of electrons is odd. When a further electron is added, it also passes into an orbital $E_g(nd)$. Since $E_g(nd)$ is degenerate, the two electrons now in this orbital may have parallel spins, and will in fact do so in order to minimise their electrostatic repulsion. Hence, with the present assumption, a co-ordinated complex with 26 valency electrons is paramagnetic, the magnetism corresponding with that of two unpaired spins.

Suppose now that A_{1g} is more stable than $E_g(nd)$. Then the 25 valency electron is again paramagnetic, the magnetism corresponding with that of one unpaired spin, but the 26 valency electron system is diamagnetic.

Measurements of the magnetic susceptibility of $[\text{Mo}(\text{CN})_8]^{4-}$, a 26 valency electron system, have been made at this College by Mr. A. Cameron. They indicate *diamagnetism*. Hence A_{1g} is more stable than $E_g(nd)$. This result at first sight is a little surprising. The probable reasons are explained in the following section.

The Relative Stability of A_{1g} and $E_g(nd)$.

According to the usual rough type of calculation of the bonding strengths of molecular orbitals, the three A_{1g} orbitals of Table I. together have zero bonding power. The secular equation, using as initial wave functions the A_{1g} orbital of the attached atoms, $A_{1g}(ns)$ and $A_{1g}(n+1s)$, is of the form

$$\begin{vmatrix} W_a - W & \alpha & \beta \\ \alpha & W_{ns} - W & 0 \\ \beta & 0 & W_{(n+1)s} - W \end{vmatrix} = 0$$

Here α and β are resonance terms, W_a represents a mean atomic energy of an electron in the vicinity of an attached atom, and W_{ns} , $W_{(n+1)s}$ are the atomic energies of an electron in the ns , $(n+1)s$ orbitals respectively of the central atom. If all three A_{1g} molecular

orbitals are filled, the contribution to the total energy of the system is simply twice that of the sum of the roots of the cubic, *viz.*, $2(W_a + W_{ns} + W_{(n+1)s})$, a quantity which does not involve α or β . A rough interpretation of this result is to say that the ns and $(n+1)s$ shells of the central atom are full, and that the A_{1g} shell of the attached atoms is also full. Thus, one of the electrons whose charge is unbalanced in the system as a whole is distributed in an orbital A_{1g} of the attached atoms (*i.e.*, one-eighth of an electron to each atom).

The secular equation for the T_{1u} orbitals is also a cubic, but now only two orbitals are filled. The most stable orbital, when filled, practically amounts to the $(np)^6$ shell, while the six electrons in the next most stable orbital will be shared more or less equally between the $(n+1)p$ orbitals of the central atom, and the T_{1u} orbitals of the attached atoms (probably with a slight tendency of the charge to accumulate in the regions of the attached atoms). Similar conclusions apply to the T_{2g} and A_{2u} molecular orbitals.

From what has been said above it appears that an eight-co-ordinated complex with 26 valency electrons is most likely to be stable if the attached atoms have a strong affinity for electrons. However, there is a counterbalancing effect, as follows.

Because of the accumulation of negative charge on the attached atoms, there will result in the neighbourhood of the central atom an intense electric field whose effect will be to undermine the stability of the $A_{2u}(nf)$ and $T_{2g}(nd)$ orbitals of the central atom. Let us approximate to this field by supposing that it arises from charges $-\alpha e$, ($0 < \alpha < 1$), situated at the corners of a cube of side d . Then the potential energy of an electron, of charge $-e$, at the point (x, y, z) , near the origin, is

$$V = 8e^2\alpha/d - C[x^4 + y^4 + z^4 - 3r^4/5] + D[x^6 + \dots] + \dots$$

where

$$r^2 = x^2 + y^2 + z^2 \quad \text{and} \quad C = 70e^2\alpha/9d^5.$$

The first term is a constant, and will affect all orbitals of the central atom equally. The total energy of the central atom will not be affected, however, because the change in the total energy of the orbitals will be cancelled out by a change in the potential energy of the positive charge of the nucleus.

The second and higher terms of V will actually cause the d, f, \dots , orbitals to separate into groups, characterised, as we have seen, by $E_g(d)$, $T_{2g}(d)$, etc., but will not shift the average position of the d orbitals, the f orbitals, etc. Now the order of magnitude of the effect of the second term to that of the third, is r^2/d^2 , *i.e.*, about 1/10. Effectively, then, we need consider only the field

$$V = C[x^4 + y^4 + z^4 - 3r^4/5].$$

The effect of this field on the d and f orbitals of the central atom may be found most simply by a method given by Penney and Schlapp.⁸ We find

$$\begin{aligned} E_g(nd) &= -3P/5, & T_{2g}(nd) &= 2P/5, & P &= 40e^2\alpha r_{nd}^4/27d^5, \\ A_{2u}(nf) &= 2Q/3, & T_{2u}(nf) &= Q/9, & T_{1u}(nf) &= -Q/3 \\ Q &= 560e^2\alpha r_{nf}^4/297d^5. \end{aligned}$$

Since P and Q are positive, $T_{2g}(nd)$ is not as stable as $E_{2g}(nd)$, and $A_{2u}(nf)$ is the least stable of the f -orbitals.

⁸ *Physic. Rev.*, 1932, 41, 194.

The order of magnitude of the quantities P and Q are difficult to estimate. One would expect them to be roughly the same as the corresponding quantities for iron-group crystals such as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, etc., *i.e.*, 2 or 3 electron-volts. Accepting these values, we see that the accumulation of negative charge on the attached atoms lowers the stability of those orbits of the central atom which are essentially concerned in the molecular binding, by amounts of the order of one or two electron volts. The effect increases with the electron-affinity of the attached atoms, but falls off rapidly (inverse fifth power) with their distance from the central atom.

The above arguments can be expressed qualitatively in terms of the pair theory. Thus, the accumulation of negative charge on the attached atoms will tend to destroy the stability of the orbits $T_{2g}(nd)$ and $A_{2u}(nf)$ of the central atom, since they are concentrated in the regions of the attached atoms. On the other hand, the orbits $E_{2g}(nd)$ and $T_{1u}(nf)$ are concentrated in the spaces between the attached atoms, and thereby minimise the Coulomb interaction with the surplus charge of the attached atoms.

The conditions for the formation of an eight-co-ordinated complex are therefore that the attached atoms, or groups, should have a strong electron-affinity, but that any additional charge which they acquire should be as far removed from the central atom as possible. These conditions are admirably fulfilled by the group CN. It is therefore significant that the only two examples which we have been able to discover of eight-co-ordination with 25 or 26 valency electrons both involve eight attached CN groups.

Summary.

Eight elements, Zr, Mo, Ru, Ce, Hf, W, Os, Th, are known to form co-ordinated complexes with eight attached atoms. With six of the eight elements, the complex has a characteristic group of 24 valency electrons. The two exceptions are Mo and W, which form complexes with groups of 25 or 26 valency electrons. These facts are shown to be predictable from the theory of molecular orbitals.

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ON THE STRUCTURE OF INSULIN.

BY D. M. WRINCH.

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Introduction.

During the past few years, there has accumulated a considerable volume of information relating to insulin, which, with advantage, could be arranged and interpreted. In this communication, therefore, an attempt is made to put together data which throw light upon the structure of insulin, and to offer interpretations of these data in terms of the cyclol theory of protein structure.¹ This theory, originally pro-

¹ D. M. Wrinch, (a) *Nature*, 1936, **137**, 411; **138**, 241 and 651; (b) *Nature*, 1937, **139**, 975; (c) *Proc. Roy. Soc., A*, 1937, **160**, 59; (d) *Science*, 1937, **85**, 566.

pounded to deal with protein films and laminate proteins, is found to imply the existence of polyhedral structures containing certain numbers of amino acid residues,² and so predicts, in general terms, the body of facts relating to the "globular" proteins established by Svedberg and his collaborators.³ The "globular" proteins have molecular weights which are not distributed at random, but fall into a sequence of widely separated classes. This is now interpreted to mean that the proteins falling into one of these classes have a common structure as regards the arrangement of the constituent amino acids, and it is further suggested that each class connotes one closed cyclol or an association of a certain number of such units.

One of these space-enclosing structures, the structure comprising 288 amino acid residues, was accordingly proposed in 1936 as the structure of molecules of egg albumin, insulin, pepsin and of the other proteins whose molecular weights are in the neighbourhood of 36,000. It is of interest that Bergmann and Niemann,⁴ state that the chemical analysis of egg albumin enables them to deduce that this molecule consists of exactly 288 residues. In the present communication the 288-structure is considered in relation to the available data for insulin.^{1d} It is found that it fits easily and elegantly with the crystallographic, chemical and physico-chemical data. It thus allows us to build a picture of the molecule, which, even if it be only very partially correct, brings many disparate facts into relation with one another, and is suggestive as regards others, which might usefully be made the objective of further researches.

Physico-chemical and X-ray Data relating to Insulin.

Insulin was first prepared in the crystalline form by Abel in 1926: the crystals belong to the rhombohedral division of the hexagonal system.⁵ Insulin crystals, by contrast with some other proteins, do not collapse on drying. Some indication of the amount of water present in the crystal lattice is afforded by the fact that the water lost by crystals heated at 104° in a vacuum is 5.35 per cent. of the air-dried weight.⁶

According to the X-ray analysis,⁷ the unit cell is rhombohedral with $a = 44.3$ A. and $\alpha = 115^\circ$, correct to about 2 per cent. This corresponds to a cell referred to hexagonal axes with $a = 74.7$ A. and $c = 30.2$ A., which is three times as big. The molecular weight corresponding to one rhombohedral cell, assuming a density of 1.315, is $39,300 \pm 800$.

Studies with the ultra-centrifuge have shown that, in a solution of p_H 4.5-7.0, insulin is isodisperse and has molecular weight^{8,9} 35,100. Its asymmetry number is 1.1, so the molecule is "globular." Comparing the two estimates of the molecular weight of insulin, it may be deduced that the rhombohedral cell contains one molecule only.

The space group of the insulin crystal is R3. The structure is of an eight co-ordination type: each molecule is surrounded by eight others,

² D. M. Wrinch, *Proc. Roy. Soc., A*, 1937, **161**, 505.

³ T. Svedberg, *J. Amer. Chem. Soc.*, 1929, *et seq.*

⁴ M. Bergmann and C. Niemann, *J. Biol. Chem.*, 1937, **118**, 301.

⁵ J. J. Abel, *Proc. Nat. Acad. Sci. U.S.A.*, 1926, **12**, 132.

⁶ J. J. Abel, E. M. K. Geiling, C. A. Rouiller, F. K. Bell and O. Wintersteiner, *J. Pharm. Exp. Ther.*, 1927, **31**, 65.

⁷ D. Crowfoot, *Nature*, 1935, **135**, 591.

⁸ B. Sjögren and T. Svedberg, *J. Amer. Chem. Soc.*, 1931, **53**, 2657.

⁹ T. Svedberg and B. Sjögren, *Nature*, 1931, **127**, 438.

two at the distance of 30.2 Å. above and below along the trigonal axis, and six at the longer distance of 44.3 Å. along the edges of the primitive rhombohedron.

The Metal Content of Insulin.

It has been found that the crystallisation of insulin is facilitated when zinc, nickel, cobalt or cadmium is present, and it is claimed that one of these substances is essential for crystallisation.¹⁰ Insulin crystals obtained in the presence of zinc were analysed and were found to contain 0.8 zinc atoms per 10,000 molecular weight of insulin¹¹: the figures for crystals obtained in the presence of cadmium and cobalt respectively gave correspondingly 0.7 cadmium atoms and 0.75 cobalt atoms. The presence of 3 metal atoms per molecule of insulin was accordingly assumed. These results are of interest in that zinc and cadmium are bivalent cations. It may be presumed that in insulin crystals cobalt also is bivalent. The fact that the number of these bivalent ions per molecule is the same and constant (within the limits of experimental error) suggests that such insulin crystals are ionic.

The fact that insulin crystallises best in the presence of these metals, not at the isoelectric point¹² p_H 5.30-5.35, but on the alkaline side¹¹ at p_H 6.0-6.2, further supports the view that the crystals are insulinates of the form A^{+2}_3 (insulin)⁻⁶, where A is a bivalent cation. The rise in p_H would then indicate the change necessary to transform insulin from its zwitterionic form into an anion with charge - 6.

The Chemical Analysis of Insulin.

The analysis of insulin, though not yet complete, gives certain indications as to its chemical composition. So far eight amino acids and one imino acid have been found among its degradation products, namely tyrosine, cystine, glutamic acid, leucine, arginine, histidine, proline and phenylalanine.¹³ The tyrosine content is high, being 12 per cent.¹⁴: so also is the cystine content which is 12 per cent., the leucine content, which is 30 per cent., and the glutamic acid content, variously estimated at 21 per cent.,^{13a} and at about 30 per cent.¹⁵ A proline content of 10 per cent. is deduced by Jensen.^{13b} An estimate of the amide nitrogen¹⁵ makes it clear that some of the glutamic acid residues found in the degradation products in the molecule are in the form of glutamine. The chemical analysis of insulin presents very considerable difficulties, and a useful check on it is available in the work on the electrometric titration of insulin¹⁶ which establishes the base-binding and acid-binding capacity of the molecule in solutions of varying p_H .

There has so far been no hint of the presence of any prosthetic group. It is probable that few, if any, amino or imino acids remain to be discovered as constituents of the molecule.

¹⁰ D. A. Scott, *Biochem. J.*, 1934, 28, 1592.

¹¹ D. A. Scott and A. M. Fisher, *ibid.*, *J.*, 1935, 29, 1048.

¹² F. O. Howitt and E. B. R. Prideaux, *Proc. Roy. Soc., B*, 1932, 112, 13.

¹³ (a) H. Jensen and O. Wintersteiner, *J. Biol. Chem.*, 1932, 97, 93; and 98, 281; (b) a private communication from Jensen, 1936.

¹⁴ V. du Vigneaud, H. Jensen and O. Wintersteiner, *J. Pharm. Exp. Ther.*, 1928, 32, 367.

¹⁵ C. R. Harington and T. H. Mead, *Biochem. J.*, 1936, 30, 1598.

¹⁶ C. R. Harington and A. Neuberger, *ibid.*, 809.

The Space-Enclosing Cyclol Molecules.

The cyclol theory postulates that the essential structural unit in proteins is the cyclol fabric (Fig. 1), a two-dimensional polycondensation

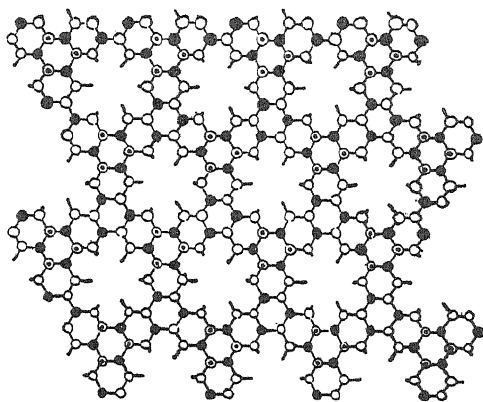


Fig. 1.

THE CYCLOL PATTERN. THE MEDIAN PLANE OF THE LAMINA IS THE PLANE OF THE PAPER. THE LAMINA HAS ITS 'FRONT' SURFACE ABOVE AND ITS 'BACK' SURFACE BELOW THE PAPER.

- = N.
- = C(OH), PEPTIDE HYDROXYL UPWARDS.
- = C(OH), PEPTIDE HYDROXYL DOWNWARDS.
- = CHR, DIRECTION OF SIDE CHAIN INITIALLY OUTWARDS.
- = CHR, DIRECTION OF SIDE CHAIN INITIALLY UPWARDS.

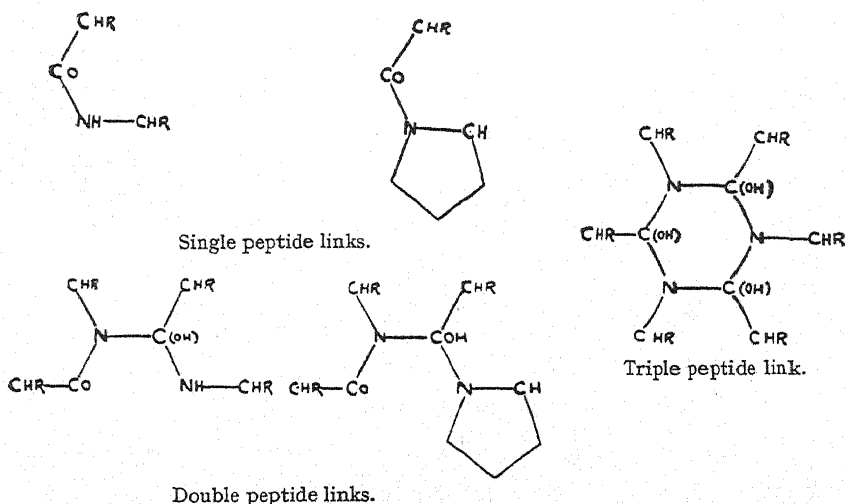


FIG. 2.

product of amino acid molecules. In this theory, Fischer's idea of a peptide link is extended to include also "multiple" peptide links (Fig. 2),

and his idea of linear polycondensations based upon peptide links is extended to cover surface polycondensations based upon multiple peptide links. This fabric may be formed by the cyclisation of polypeptides (Fig. 3), the polymerisation of substituted diketopiperazine molecules

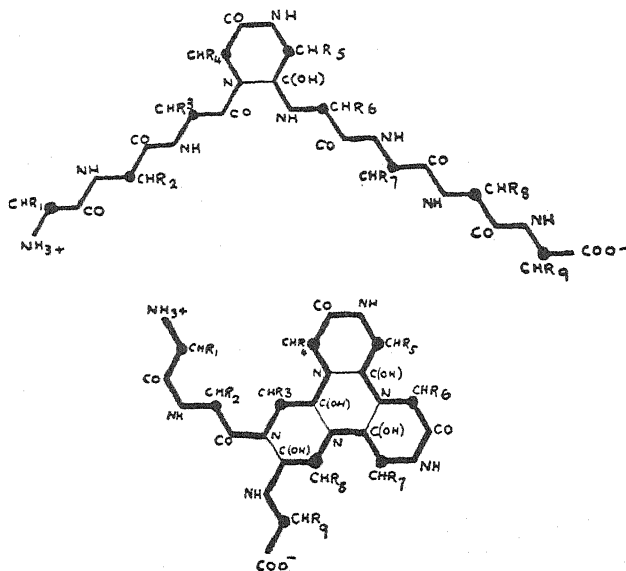


FIG. 3.

(Fig. 4) or directly by polycondensation of amino acid molecules (Fig. 5). By bending about one line after another, certain pieces of this fabric can join up and so enclose a portion of space. Space-enclosing cyclol molecules can therefore be constructed which consist of certain special numbers of residues. A series $C_1, C_2, \dots, C_n, \dots$ comprising 72, 288, $\dots, 72n^2, \dots$ amino acid residues has been constructed.

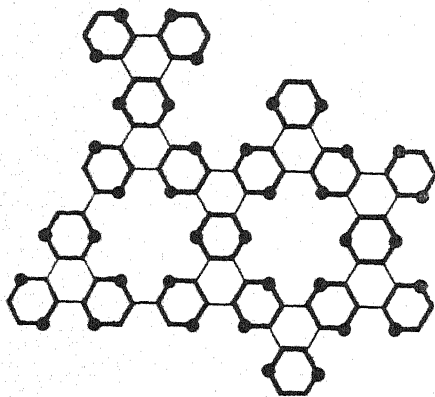


FIG. 4.—A diketopiperazine polymer.

The molecular weight of insulin is known accurately enough for it to be plain that C_1 is much too light and C_3 is much too heavy. The only cyclol of the series which comes into question is therefore C_2 . Here the number of residues—288—is certainly of the right order of magnitude, and is, in fact, the number claimed for egg albumin.⁴ Also, since this structure, like all C_n structures, is simply a condensation of amino acid molecules, no prosthetic group is required. Furthermore, the polyhedral character of this molecule is in accord with, and offers an interpretation of, the "globularity" of the molecule.

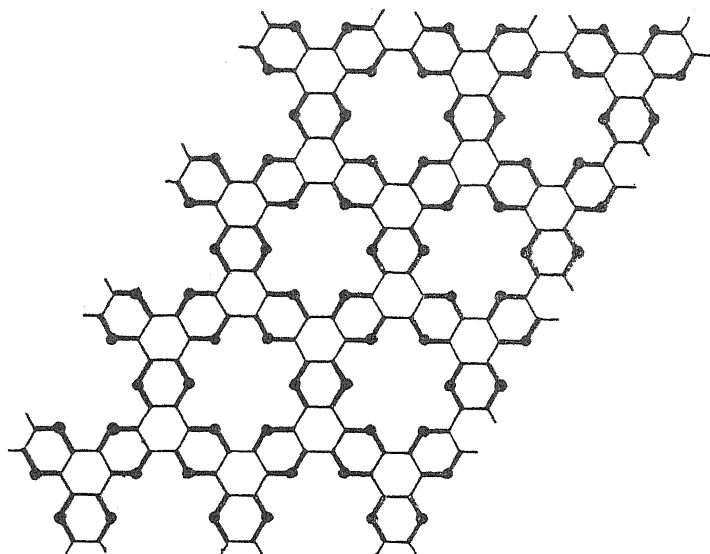


FIG. 5.—Surface polycondensation of amino acids.

The Detailed Structure of C_2 .

The detailed structure of C_2 is simple in essentials. The structure of the C_n molecules has been discussed in earlier publications of this series.^{1b, d, 2} For convenience of exposition, the cyclol

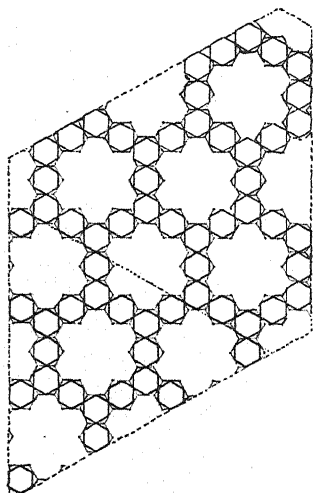


FIG. 6.—A portion of the cyclol fabric representing one hexagonal and one triangular face of the C_2 molecule, *i.e.* one quarter of the portion of fabric making one C_2 molecule. The carbons bearing R groups are indicated by dots.

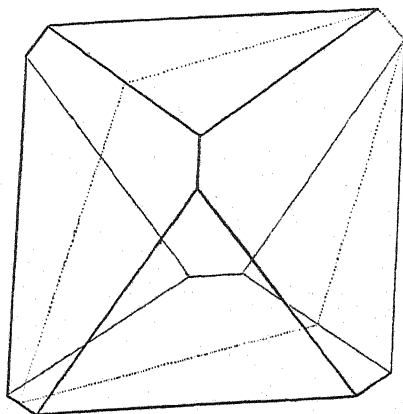


FIG. 7.—The polyhedral frame of the C_2 molecule.

fabric (Fig. 1) may be replaced by its median network (Fig. 6) in which the C—C—N atoms of the constituent residues are replaced by points midway between linked atoms. The median networks of all the C_n molecules lie on the plane faces of truncated tetrahedra and so have four plane hexagonal faces, H, h, \dots and four plane triangular faces, T, t, \dots . Fig. 7 shows the polyhedral frame of the molecule C_2 —the

truncated tetrahedron on which the median network of C_2 lies. The original tetrahedron is of side $45c$, and from it four tetrahedra of side $21c$ have been cut off, leaving a truncated tetrahedron with four triangular faces with side $p = 21c$ and four hexagonal faces with sides alternating between $p = 21c$ and $q = 3c$. To understand the structure of the molecules it is worth while to consider also the network as it appears when it is slit along some edges and hinged along the others and then opened out flat. Fig. 6 shows one quarter of the median network corresponding to the complete fabric of the molecule C_2 under these circumstances, and pictures one triangular face with centre t and one hexagonal face with centre H . The positions of the C—C—N atoms are also indicated on this diagram, the positions of the carbon atoms bearing R groups (*i.e.* amino acid side chains) being specially indicated. Fig. 8 shows photographs of a model of the complete median network of a C_2 molecule.

It should again be emphasised that data to enable us to decide upon the sides and angles of the hexagons in the cyclol fabric are at present lacking. The C—C distance in diamond is 1.54 \AA , the C—N distance in hexamethylene tetramine¹⁷ is 1.42 \AA . Further, the valency angle for C in diamond is the tetrahedral angle

$$\cos^{-1}(-1/3) = 109^\circ 28' 16''.$$

The valency angle for N is also the tetrahedral angle in hexamethylene tetramine, in which, as in the cyclols, each N atom is linked to three C atoms, though it takes other values in a number of compounds in which it is not so linked. In these circumstances it is considered reasonable to adopt a mean value $a = 1.50 \text{ \AA}$ for the C—C and C—N links indifferently (and consequently $c = \sqrt{6}a/3 = \frac{1}{2}\sqrt{6}a$) and the value δ for the valency angle of C and of N.

Now the molecule C_2 , apart from its side chains, has four trigonal axes, HT, ht, . . . each the central normal of one triangular face T, t, . . . and of the hexagonal face H, h, . . . opposite to it. These axes are concurrent in O, the orthocentre of the polyhedron. Fig. 9 shows the projection on the plane containing two trigonal axes HT, ht of the polyhedral frame of the molecule. This figure may be compared with Fig. 7 and also Fig. 8*b* in which the projection of the complete median network of the molecule on such a plane is seen. The actual distances associated with C_2 molecules, as shown in Fig. 9, are as follows:

$$ht = HT = (p + q) \sin(\pi/3) \sin \delta = 24c\sqrt{2}/\sqrt{3} = 16a = 24 \text{ \AA}.$$

The distance between P and Q, the midpoints of diametrically opposite short sides of length q is

$$PQ = (p + 2q)/\sqrt{2} = 45c/\sqrt{2} = 15a\sqrt{3} = 38.97 \text{ \AA}.$$

The lines joining such points form three mutually perpendicular axes and the angle between any of these and a trigonal axis of the molecule is $\delta/2$. Further,

$$hO = HO = PQ \cos(\delta/2)/2 = 15c\sqrt{6}/4 = 15a/2 = 11.25 \text{ \AA},$$

$$tO = TO = TH - OH = 12.75 \text{ \AA}.$$

¹⁷ (a) R. G. Dickinson and A. L. Raymond, *J. Amer. Chem. Soc.*, 1923, 45, 22; (b) R. W. G. Wyckoff and R. E. Corey, 1934.

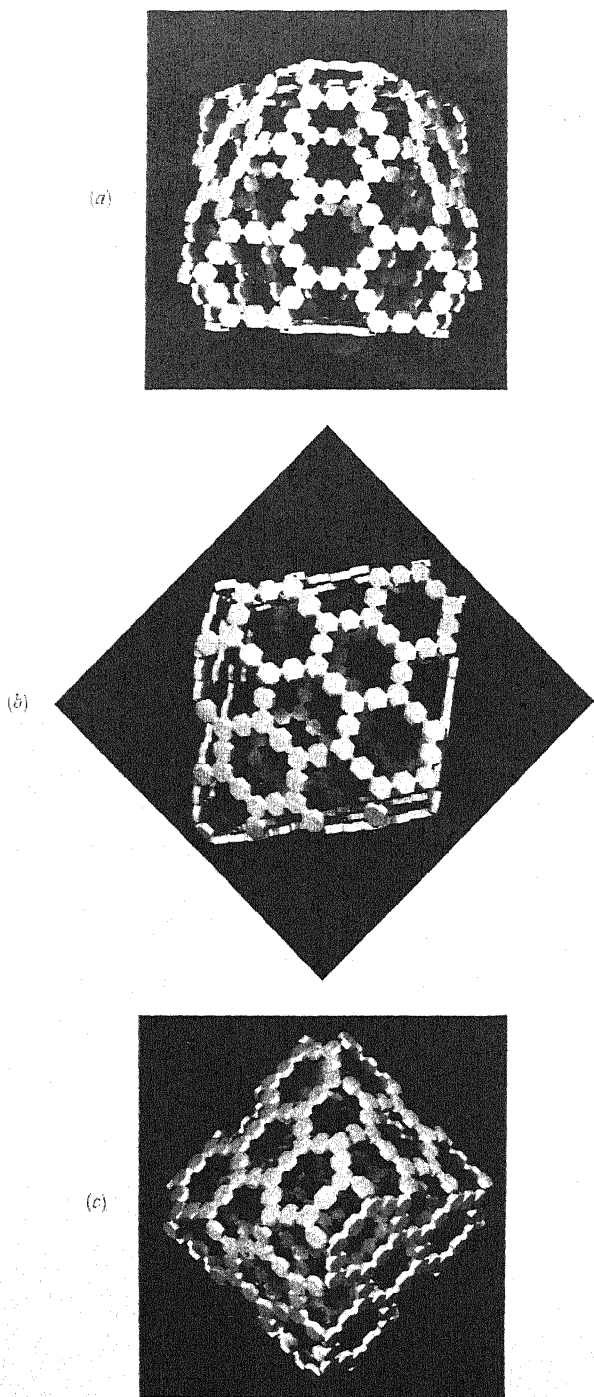


FIG. 8.—Three views of the median framework of a C_2 molecule.
 [To face p. 1375.]

[So far we have proceeded strictly in accordance with the metrical conditions stated above and the frames of the resulting C_n space-enclosing cyclols are truncated tetrahedra. These frames can, if required, be converted into truncated octahedra by a parallel displacement of faces which leaves the number of residues per molecule unchanged].

The Capacity of Megamolecules to Form Crystals.

The capacity of any molecule to form a crystal is dependent upon its capacity to form extramolecular links. These links may be of a variety of types, representing forces of different magnitudes, ranging from van der Waals forces through the comparatively small forces due to electrostatic attractions in hydroxyl and hydrogen bonds, to the larger forces due to the electrostatic attractions in salt linkages. (Covalent links, as in the diamond lattice, are not mentioned, since such a lattice is, strictly speaking, one single megamolecule). Now the links between megamolecules are of the same nature as those between small molecules. The fact that a megamolecule forms a crystal lattice, therefore, indicates that its structure allows the simultaneous formation of a number of links whose aggregate strength is adequate to the mass of the molecules.

Now the simultaneous formation of many links between one megamolecule and its neighbours is evidently facilitated if the molecules have a polyhedral character, since then faces of considerable area or edges of considerable length can be apposed. Megamolecules which form crystals, I would suggest, must in general have a polyhedral character. This is well exemplified in the cyclol molecules, whose geometrical characteristics at once suggest that they may form crystals by the apposition of faces or edges. If there is HH or TT apposition the co-ordination number is 4: if HH and TT or HT it is 8. If edges be apposed, the co-ordination number is 12. The conditions for crystallisation are evidently particularly favourable if, as in the case of the cyclol molecules, each molecule is simply a fabric bent round to join up. In such a case the total area of the faces of a molecule is directly proportional to the molecular weight. The numbers of intermolecular links in a $C_1, C_2, \dots C_n, \dots$ lattice (e.g.) can then be proportional to the number of residues per molecule so that the stability of the corresponding megamolecular lattice is independent of the size of the constituent molecules.

The C_2 Molecule and the Unit Cell of Insulin.

It is now necessary to investigate whether or not the C_2 space-enclosing cyclol molecules can build a lattice whose space group is R_3 : whether they fit the rhombohedral cell $a = 44.3$, $\alpha = 115^\circ$, so that each molecule has two neighbours at the distance 30.2 A. above and below along the trigonal axis and six neighbours at distances 44.3 A. along the edges of the primitive rhombohedron: and in the event of these requirements being satisfied, whether any light is thrown by the structure of C_2 upon the actual mechanism of intermolecular co-ordination. The fact that C_2 has (apart from its R groups) four trigonal axes, shows that this molecule can build a lattice whose space group is R_3 . To make C_2 trigonal, it is sufficient to impose two conditions. First, the arrangement of residues in one hexagonal face H and one triangular face T shall be trigonal, so that the faces are unchanged when they are rotated through $\pm 2\pi/3$ about the HT axis. Secondly, the other three hexagonal faces, h, shall all be made up of the same residues arranged in the same manner,

and similarly the three triangular faces t , so that here too nothing is changed when the molecule is rotated through $\pm 2\pi/3$ about the HT axis. The molecule therefore then has two trigonally symmetric faces H and T, three identical hexagonal faces h, h, h , and three identical triangular faces t, t, t . These restrictions are of interest from the point of view of the chemical analysis: they imply in particular that the number of each type of residue must be a multiple of 3.

[It is, however, possible that the molecule itself need not be strictly trigonal in relation to the R-distribution.]

Now the unit rhombohedral cell of the crystal contains one molecule of insulin only: the hexagonal cell, correspondingly, three. We may therefore put at each vertex of the rhombohedron the orthocentre of a C_2 molecule, arranging them all in the same orientation, so that each molecule has one pair of faces HT normal to the trigonal axis and the three other pairs normal respectively to the three directions tetra-

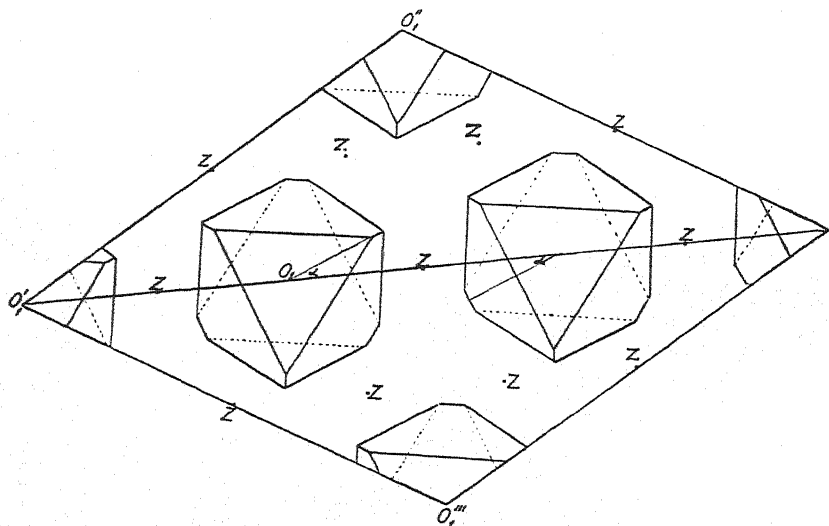


FIG. 10.— C_2 molecules arranged in the hexagonal cell of the insulin lattice.

hedrally inclined to the trigonal axis. The only point to consider is then the orientation of each molecule with respect to the lines joining its orthocentre O_1 to the orthocentres O_1', O_1'', O_1''' , at the neighbouring vertices of the primitive rhombohedron. In other words, the only outstanding point is the value of the angle α in the hexagonal cell shown in Fig. 10, a datum which should in due course be deducible from X-ray studies of insulin crystals. The hexagonal cell has $O_1' O_1'' = 74.7$ A. and $O_1' O_1 = 74.7/\sqrt{3} = 43.13$ A. (Zinc ions are placed midway between orthocentres of co-ordinated molecules.)

Fig. 11 shows the arrangement of the molecules in the rhombohedral cell in the particular case when α is zero. (Zinc ions are placed midway between co-ordinated faces.) It shows the projections of the molecules 1, 2, 1', 2', on a plane containing $O_1 O_2$, the trigonal axis, and $O_1 O_1', O_2 O_2'$, one pair of opposite edges of the rhombohedron. It can be modified to cover the case when α has any specified value without difficulty.

With this arrangement the molecule has its trigonal face H_1 in apposition to the trigonal face T_2 of molecule 2: its three identical faces h_1 are in apposition to the three identical faces t_1', t_1'', t_1''' , belonging to the molecules $1', 1'', 1'''$. The distance $O_1O_2 = c = 30.2$ A. and

$$O_1m_1 = m_1m_2 = m_2O_2 = 30.2/3 = 10.13 \text{ A.}$$

The distance

$$O_1O_1' = O_2O_2' = 44.3 \text{ A. and } O_1'm_1 = m_2O_2' = a/\sqrt{3} = 74.7/\sqrt{3} = 43.13 \text{ A.}$$

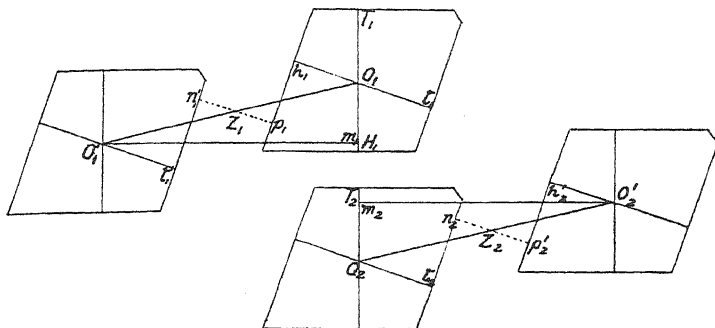


FIG. 11.— C_2 molecules arranged in the rhombohedral cell of the insulin lattice.

The distance between HT faces is

$$T_2H_1 = O_1O_2 - T_1H_1 = 30.2 - 24 = 6.2 \text{ A.,}$$

and the orthocentres O_1 and O_2 are necessarily aligned along the trigonal axis. The distance between ht faces is

$$\begin{aligned} n_1'p_1 &= a/\sqrt{3} \cdot \sin \delta \cdot \cos \alpha + c/3 \cdot \cos \delta - 24 \text{ A.} \\ &= 40.66 \cos \alpha - 3.35 - 24 \\ &= 13.3 - 40.66 (1 - \cos \alpha) \\ &= 13.3, 13.16, 13.68, 11.93, 10.86, 9.50, 7.87 \text{ A., } \dots \end{aligned}$$

when $\alpha = 0^\circ, 5^\circ, 10^\circ, 15^\circ, 20^\circ, 25^\circ, 30^\circ, \dots$

The faces h, t are not centrally aligned either along the axes $O_1h_1, O_1't_1'$, or (unless α is zero) along axes perpendicular to these.

The Mechanism of Co-ordination between Insulin Molecules in the Crystal Lattice.

The faces HT which are responsible for the co-ordination of molecules along the trigonal axis are parallel and at a distance 6.2 A. apart. A consideration of the structure of halloysite¹⁸ then makes it plausible to suppose that linking is by means of hydroxyls, provided that the actual measurements tally. Halloysite has a layer structure in which the complete repeat of layers is represented by $3O, 2Si, 2OH, 3OH, 2Al, 3OH$ and the distance between the layers of opposed hydroxyls is about 3 A.

If hydroxyl links provide the mechanism of HT co-ordination, the distance of hydroxyls from the median faces should therefore be $(6.2 - 3)/2 = 1.6$ A., a distance which suggests that peptide carbon hydroxyls come into question. The distance of peptide carbon atoms from the faces is $a/6 = 0.25$ A., leaving 1.35 A. for the distance C—OH.

¹⁸ M. Mehmel, *Z. Krist.*, 1935, 90, 35.

This measurement, when compared with the C—OH distance of 1.35 Å. in resorcinol¹⁹ and 1.46 Å. in certain alcohols²⁰ makes the proposed mechanism highly plausible, especially in view of the fact that the considerable area of the co-ordinated faces allows the simultaneous linking of a number of hydroxyls. The mechanism of co-ordination now suggested applies, not only to the closed cyclols at present under discussion which possess 8 faces lying on a polyhedron, but also to the open cyclols possessing, as it were, a single face. It explains the back-to-back type of co-ordination of multilaminar protein aggregates, which, in view of the structure of the clay minerals, was already suggested for consideration in the first publication of this series,^{1a} and which has since been realised in a series of experiments designed to test the cyclol hypothesis.²¹

Other possible mechanisms of HT co-ordination will be considered later, when the chemical composition of insulin is more nearly known. We may instance the dimeric association of glutamine molecules, after the manner of the association of CO, NH groups in isatin.²²

The co-ordination of ht faces is rather different in character. The interface distance is larger: it ranges from 13.3 Å., when $\alpha = 0$, to 7.87 Å., when $\alpha = 30^\circ$ This indicates co-ordination by means of R groups belonging to residues located in the apposed faces. These faces are not centrally aligned (as in the case of HT faces) either along the axes O_1h_1 and $O_1't_1'$ or (if α is not zero) along axes perpendicular to these: this indicates that the residues actually involved are located only in part of the ht faces. It is then to be expected that no considerable number of groups is involved.

The stoichiometric relation between insulin content and the content of zinc (or other metal) in the crystal lattice points to the same conclusion, since it may be supposed that one zinc ion only is involved in each ht co-ordination. In this way each molecule will have a half share of each of six ions, giving a total of three ions for each molecule of insulin, as required. Further, the number of side chains involved in each ht co-ordination will be small.

It has already been suggested that these ions should form salt linkages with free carboxyl groups belonging to the insulin molecule (Scott and Fisher, 1935). These can be carried by glutamic acid residues. Alternatively, it may be suggested that the phenolic groups of tyrosines are involved. These types of co-ordination throw light upon the difficulty (or impossibility) of crystallising insulin in the absence of bivalent cations and also explain the fact that insulin crystals (unlike pepsin crystals) do not collapse in the absence of water. As remarked by Scott and Fisher in 1935 "crystalline insulin contains the metals as chemically combined constituents and not as impurities." If the insulin lattice is essentially an ionic lattice (Insulin A_3), where A represents the bivalent cation, the stability of the lattice depends partly upon salt linkages with the metal cations.

We consider first the possibility of zinc ions being in salt linkage with carboxyl groups of glutamic acid molecules. The distance between the C_β and the carbon of the carboxyl groups $C_\alpha OOH$ is 1.79 Å. along the

¹⁹ J. M. Robertson, *Z. Krist.*, 1934, 89, 318; *Nature*, 1935, 136, 755.

²⁰ E. G. Cox, *Proc. Roy. Soc., A*, 1937 (*in the press*).

²¹ I. Langmuir, V. Schaefer and D. M. Wrinch, *Science*, 1937, 85, 76.

²² E. G. Cox, T. H. Goodwin and A. I. Wagstaff, *Proc. Roy. Soc., A*, 1936, 157, 399.

direction C_γ to C_δ , so that, assuming a distance of, say, 3.3 Å. between the line joining one pair of oxygens (surrounding the zinc ion) and the line joining the other pair of oxygens (forming with the first pair a tetrahedral environment of oxygens for the zinc ion), the distance from C_γ of one molecule and C_γ of the neighbouring molecule is

$$1.79 + 3.3 + 1.79 = 6.88 \text{ Å.}$$

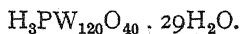
The interface distance is $13.3 - 40.66(1 - \cos \alpha)$. A consideration of the dimensions of the R groups of glutamic acid thus shows that salt linkages between a zinc ion and two carboxyl groups are geometrically possible, and indicate that α is, say, 10° - 20° .

It is also geometrically possible to postulate that the zinc ions are linked with ionised phenolic groups of tyrosine if α is practically zero. But the dissociation constants of these groups is not sufficiently high to allow the ionisation of these groups at the required p_H of 6.0-6.2. It then appears that if the molecules are linked by means of zinc ions, this linking can only be due to the carboxyl groups of glutamic acid molecules and that, in consequence, it may be expected that α is not zero.

The Water Content in Insulin Crystals.

When large units such as C_2 space-enclosing cyclol molecules build a crystal lattice, there will necessarily be considerable spaces which are not tenanted by the actual atoms composing the molecules, or by foreign ions helping to bind the molecules together. Extramolecular spaces may be seen in Figs. 10 and 11: but there may also be intramolecular spaces within the median networks of the cyclol molecules.

Now water molecules are known to act as intermediaries between polar groups. In the crystal of oxalic acid dihydrate²³ water molecules bind together the carboxyl groups of the molecules. They are known to form clusters of considerable size, such as the clusters $(H_3 \cdot 29H_2O)^{+8}$ in the beautiful structure²⁴ of



They fill considerable spaces between layers in the case of montmorillonite.²⁵ It may be presumed that all the spaces in the C_2 lattice are similarly filled by water molecules in orderly array, so that the crystal is severely crystalline throughout. The large number of peptide hydroxyls carried by the cyclol fabric (amounting to one per residue) will here play an important part, since in no possible arrangement can all these groups-be linked to one another and to one another alone.

It may be deduced that insulin crystals contain a considerable complement of water molecules. The fact that insulin crystals heated in a vacuum at 104° lost water corresponding to 5.35 per cent. of the air-dried weight⁶ calls attention to the existence of something of the order of 100 water molecules per insulin molecule. It is possible that even after this treatment the insulin molecules may have some water molecules associated with them. An estimate of the full complement of water molecules per molecule in the crystalline insulin is urgently required. Such an estimate would prove an excellent check on the present structure, since the approximate extent of the spaces available

²³ W. H. Zachariasen, *Z. Krist.*, 1934, **89**, 442.

²⁴ A. J. Bradley and J. W. Illingworth, *Proc. Roy. Soc., A*, 1936, **157**, 113.

²⁵ U. Hofmann, *Koll. Z.*, 1934, **69**, 351.

for them can be calculated. Further, without it it is not possible to deduce from the analysis of the hydrolytic products of insulin the number of each type of residue present in the insulin molecule. In view of the large amount of space available for water molecules in the lattice, it appears likely that many, if not all, the water molecules needed to change the amino acid residues in the insulin molecules into the corresponding amino and imino acid molecules in the hydrolysate may be supplied by the water molecules already present in the lattice.

Conclusions.

In view of the detailed investigation given in this paper, the closed cyclol C_2 is proposed as the structure of insulin for the following reasons :

1. Any C_n space-enclosing cyclol molecule, in view of its polyhedral character, offers an interpretation of the "globular" character insulin is known to possess. In accordance with the chemical evidence, it is simply a condensation product of amino acid molecules and contains no prosthetic group.

2. Any C_n space-enclosing cyclol molecule by its geometry explains the 8-co-ordination pattern in insulin crystals in terms of the apposition of faces. The trigonal nature of the lattice (if it is to be taken to imply a strictly trigonal character for the molecules) is easily translated into terms of the arrangement of residues of the various types in the piece of cyclol fabric of which it is composed.

3. The C_2 molecule comprising 288 residues has a molecular weight which is of the right order of magnitude for insulin.

4. The dimensions of the C_n molecules are derived by purely geometrical reasoning from the original hypothesis of the cyclol theory, and are in no sense introduced *ad hoc*. The C_2 molecule fits easily into the unit rhombohedral cell given by the X-ray analysis of insulin crystals : in doing so it suggests possible mechanisms of co-ordination between molecules.

Summary.

A structure is proposed for the molecule of insulin. This structure consists of a portion of the cyclol fabric bent round to enclose a portion of space. In accordance with the chemical evidence, it is simply a condensation product of amino acid molecules and contains no prosthetic group. Its molecular weight is of the right order of magnitude. Its polyhedral character offers an interpretation of the "globular" character insulin is known to possess, and explains the 8-co-ordination pattern in insulin crystals in terms of the apposition of faces. The dimensions of the molecule, which are derived by purely geometrical reasoning from the original hypothesis of the cyclol theory, and are thus in no sense introduced *ad hoc*, show that it fits easily into the unit rhombohedral cell given by the X-ray analysis of insulin crystals and in doing so suggests possible mechanisms of co-ordination between molecules.

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THE RELATION BETWEEN REFRACTION DATA AND REACTIVITY OF HALOGENATED METHANE DERIVATIVES.

By J. M. STEVELS.

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Polanyi and co-workers,¹ in their investigations on the reaction of sodium vapour and hydrogen with many halogenated organic compounds, indicated the modification of the collision number of these reactions (*i.e.*, the number of collisions which must take place on the average before one is effective). The higher the collision number, the greater is the energy of activation of the reaction. The halogen compounds which show the least energy of activation are those in which the halogen ions are most weakly bound. This becomes apparent when we compare these phenomena with the vibration frequencies of the ions. The restoring force constant is a criterion for the strength of the bond: the lower this constant, the weaker the bond of the ion in question. The energy of activation and the restoring force constant are thus directly related, as has been pointed out by Polanyi and co-workers.^{1c,2}

On the other hand, the refraction is also a criterion for the strength of the bond. According to the deformation scheme of Fajans and Joos³ the refraction of a particular ion will decrease when the ion is more strongly bound. When it is in a stronger electrostatic field the ion is more polarised and therefore less polarisable; according to these authors we may regard the refraction for the D-line as a criterion for the polarisability, so long as the D-line is far enough in the spectrum from the infra-red absorption on the one hand, and from the ultra-violet on the other. We shall, therefore, assume with Fajans and Joos that the D-line completely describes the polarisability of the ion in question.* We also know, that, according to Wolf and Herzfeld⁴ it is not the electrostatic field that determines the polarisability, but the energy of the bond. In our research the schemes of Fajans and Joos and of Wolf and Herzfeld entirely support one another.

We have accurately measured the refractive indices and densities of the various liquid halogenated methane derivatives; the results⁵ are given in Table I.

The refractive indices were all measured to within 5 decimal places, the densities to within 4, but, as possible errors may occur in the last

* How far this scheme applies also to the H_{α} - and the H_{β} -line and to the wave-length extrapolated to infinity is discussed elsewhere.⁵

¹ (a) H. von Hartel and M. Polanyi, *Z. physik. Chem.*, B, 1930, 11, 97; (b) H. von Hartel, N. Meer, and M. Polanyi, *ibid.*, 1932, 19, 139; (c) W. Heller and M. Polanyi, *Trans. Faraday Society*, 1936, 32, 633.

² R. A. Ogg and M. Polanyi, *ibid.*, 1935, 31, 482.

³ K. Fajans and G. Joos, *Z. Physik*, 1924, 23, 1.

⁴ K. F. Herzfeld and K. L. Wolf, *Ann. d. Physik*, 1925, 78, 35; 1925, 78, 195.

⁵ For further details information will be given in J. M. Stevels' *Thesis*, Leiden, 1937.

decimals, the results are given only to 4 and 3 places respectively. The molecular refractions are calculated from the original data. Both density and refractive index are determined at 20° C. with the exception of CHCl_2F which was determined at 9° because its boiling-point is 14.5° C.

TABLE I.

	M.	d_4^{20} = Density.	n_D^{20} .	$[R_D] = \frac{n^2-1}{n^2+2} \frac{M}{d}$.
CH_2Cl_2	84.94	1.324	1.4244	16.38
CHCl_2F	102.92	1.405	1.3724	16.67
CHCl_3	119.39	1.489	1.4456	21.37
CCl_3F	137.37	1.490	1.3849	21.61
CCl_4	153.84	1.594	1.4603	26.44
CH_2ClBr	129.39	1.944	1.4841	19.04
CHCl_2Br	163.85	1.980	1.4964	24.19
CCl_3Br	198.29	2.012	1.5061	29.29
CH_2Br_2	173.85	2.496	1.5419	21.92
CHBr_2F	191.84	2.421	1.4685	22.05
CHClBr_2	208.30	2.451	1.5482	27.00
CHBr_3	252.76	2.890	1.5977	29.83
CFBr_3	270.75	2.757	1.5256	30.12
CBr_4	331.66	—	—	39.00
CH_3I	141.95	2.279	1.5312	19.28
CH_2FI	159.95	2.366	1.4911	19.58
CH_3CI	176.40	2.422	1.5822	24.31
CHCl_2I	210.85	2.392	1.5840	29.50
CCl_3I	245.30	2.355	1.5854	34.94
CH_2I_2	267.88	3.320	1.7411	32.58
CHI_3	393.80	—	—	48.55

The values of CBr_4 and CHI_3 are determined from measurements of mixtures in various solvents. The refraction values of the other substances may be regarded as determined to an accuracy of 2°/100.

We now consider the bond refractions, *i.e.*, in respect of every refraction value found we consider four parts of which each must be attributed to a particular bond. This corresponds, thus, to the "atomic refraction" of the halogen ion in question added to $\frac{1}{4}$ of the "atomic refraction" of the C ion. Generally speaking, therefore, we must assume that the refraction of a hydrogen or halogen ion is different in the various halogenated methane derivatives; we shall fully develop below the classification of the variations found in the refraction values.

Take the series CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl , CH_4 . We assume that the molecular refraction is additively made up of the bond refractions, as follows directly from the scheme of Fajans and Joos, but we definitely abandon the supposition that these bond refractions are constant.

In CCl_4 a chlorine ion is placed in the field of the central C ion which is counteracted by 3 other chlorine ions. We represent the bond refraction of this chlorine ion by ClClClCl . This chlorine ion is naturally influenced by the other molecules, but we shall revert to this point later.

$$[\text{RCCl}_4] = 4\text{ClClClCl}.$$

In CHCl_3 we may represent the refraction of the chlorine ion by ClClClH , and that of the hydrogen ion by HClClCl and, thus,

$$[\text{RCHCl}_3] = 3\text{ClClClH} + \text{HClClCl}.$$

By analogy

$$[\text{RCH}_2\text{Cl}_2] = 2\text{ClClHH} + 2\text{HClCl},$$

$$[\text{RCH}_3\text{Cl}] = \text{ClHHH} + 3\text{HClH},$$

$$[\text{RCH}_4] = 4\text{HHHH}.$$

We have now to determine these values separately. In the most favourable circumstances there are in such a series five known quantities (the R 's), while there are 8 unknown. As the differences between the different Cl and H values are small, however, as will be shown later, we may make the assumption that ClClClCl , ClClClH , ClClHH and ClHHH form an arithmetical series and therefore generally speaking

$$\text{ClCl}_{(3-a)\text{H}_a} = \text{ClClClCl} + a\Delta_{\text{Cl}}^{\text{H}},$$

$\Delta_{\text{Cl}}^{\text{H}}$ is thus the change in refraction which takes places in one chlorine ion by replacing another chlorine ion by a hydrogen ion. By analogy we write

$$\text{H}_{\text{H}(3-a)\text{Cl}_a} = \text{HHHH} + a\Delta_{\text{H}}^{\text{Cl}}.$$

We shall now abbreviate ClClClCl to Cl and in general X_{xxx} to X. X, thus, represents the refraction of the X ion in the compound CX_4 .

If we include the above in our equation we then have

$$\begin{aligned} [\text{RCCl}_4] &= 4\text{Cl} \\ [\text{RCHCl}_3] &= 3\text{Cl} + 3\Delta_{\text{Cl}}^{\text{H}} + \text{H} + 3\Delta_{\text{H}}^{\text{Cl}} \\ [\text{RCH}_2\text{Cl}_2] &= 2\text{Cl} + 4\Delta_{\text{Cl}}^{\text{H}} + 2\text{H} + 4\Delta_{\text{H}}^{\text{Cl}} \\ [\text{RCH}_3\text{Cl}] &= \text{Cl} + 3\Delta_{\text{Cl}}^{\text{H}} + 3\text{H} + 3\Delta_{\text{H}}^{\text{Cl}} \\ [\text{RCH}_4] &= 4\text{H}. \end{aligned}$$

The coefficients of Δ are obtained by multiplying the number of ions which undergo the change by the number of ions which exercise their influence. The coefficient of $\Delta_{\text{Cl}}^{\text{H}}$ is always, clearly, the same as that of $\Delta_{\text{H}}^{\text{Cl}}$. We can now include $\Delta_{\text{Cl}}^{\text{H}} + \Delta_{\text{H}}^{\text{Cl}}$ in one symbol, *viz.*,

$$\Delta_{\text{Cl}}^{\text{H}} + \Delta_{\text{H}}^{\text{Cl}} = (\text{HCl})$$

(HCl) is the result of the mutual action of the ions H and Cl and our equations now become

$$\begin{aligned} [\text{RCCl}_4] &= 4\text{Cl} \\ [\text{RCHCl}_3] &= 3\text{Cl} + \text{H} + 3(\text{HCl}) \\ [\text{RCH}_2\text{Cl}_2] &= 2\text{Cl} + 2\text{H} + 4(\text{HCl}) \\ [\text{RCH}_3\text{Cl}] &= \text{Cl} + 3\text{H} + 3(\text{HCl}) \\ [\text{RCH}_4] &= 4\text{H}. \end{aligned}$$

We see here that from 5 data we only need to calculate 3 unknowns. This has the dual advantage that we can, to some extent check, our assumption as to the linear course of the refraction value of chlorine and hydrogen in this series, while, on the other hand, where only 3 or 4 values of the R 's are known we can still reach a result.

We cannot expect of course that the (XY) symbols can always be determined to within 2 decimals, as may be done for [R], because many other influences (dipole actions, etc.) are included in the (XY) values. In many cases, however, fairly accurate determination is possible. Important conclusions may be drawn from its sign and order of magnitude. Consider, now, the most general case, the building up of the refraction of CXYZW . Obviously

$$\begin{aligned} [\text{Rcxyzw}] &= \text{X} + \Delta_{\text{X}}^{\text{Y}} + \Delta_{\text{X}}^{\text{Z}} + \Delta_{\text{X}}^{\text{W}} \\ &\quad + \text{Y} + \Delta_{\text{Y}}^{\text{X}} \quad \quad \quad + \Delta_{\text{Y}}^{\text{Z}} + \Delta_{\text{Y}}^{\text{W}} \\ &\quad + \text{Z} \quad \quad \quad + \Delta_{\text{Z}}^{\text{X}} \quad \quad \quad + \Delta_{\text{Z}}^{\text{Y}} \quad \quad \quad + \Delta_{\text{Z}}^{\text{W}} \\ &\quad + \text{W} \quad \quad \quad + \Delta_{\text{W}}^{\text{X}} \quad \quad \quad + \Delta_{\text{W}}^{\text{Y}} + \Delta_{\text{W}}^{\text{Z}} \end{aligned}$$

so that

$$[\text{Rcxyzw}] = \text{X} + \text{Y} + \text{Z} + \text{W} + (\text{XY}) + (\text{XZ}) + (\text{XW}) + \frac{(\text{YZ}) + (\text{YW}) + (\text{WZ})}{2}$$

or, more general

$$[R_{C X_1 X_2 X_3 X_4}] = \sum_1^4 X_n + \frac{1}{2} \sum_{\substack{n=1 \\ m=1}}^4 (X_n X_m)$$

in which $(X_n X_m) = 0$ for $n = m$.

One great disadvantage of this method of description is that we can never determine $\Delta_{X_n}^m$ separately. As will appear later, however, we can say, at any rate approximately, what part of $(X_n X_m)$ is derived from $\Delta_{X_n}^m$ and what from $\Delta_{X_m}^n$.

All measurements were made with compounds in a liquid state, but the mutual influence of the molecules exerted no confusing influence, however, as may be seen from the following: Let us take an ion X_n : this lies in the field of the central C ion, which is counteracted by other ions of the same molecule. X_n , however, constantly comes into the neighbourhood of ions of other molecules and statistically it will come near to an ion X_m of another molecule just as frequently as the molecule itself carries X_m ions. The negative ions of the other molecules strengthen the field of the central ion of the molecule in question, which they polarise in the sense that the polarisation due to the central ion is increased.

$\Delta_{X_n}^m$ thus represents the modification of the refraction of the ion X_n by the presence of the ion X_m , whether X_m be in the molecule itself or in other molecules. In the gaseous condition, obviously the latter influence is almost absent, and, the X_n ion being here in a less strong field, its refraction will be higher. This applies to innumerable non-polar substances and especially to those for which we assume for the molecule a tetrahedron form, as Fajans and Joos³ have already pointed out. The difference between the refraction in the gaseous and liquid condition is always extremely small. We may therefore conclude that the influence of the "other molecules" upon the refraction in the liquid state is very small.

We calculate now the mutual actions from our refraction data. For the sake of brevity we give here only an example of the calculation of (HCl). The other $(X_n X_m)$ values are obtained in an analogous way. The values found in this way fit the mixed halogen methane derivatives also.⁵ The refractions of CH_2Cl_2 , $CHCl_3$ and CCl_4 are known in a liquid state. If we assume for $[R_{CH_4}]$ the value 6.60⁶ we find the equations

$$4H = 6.60 \quad . \quad . \quad (1)$$

$$2Cl + 2H + 4(HCl) = 16.38 \quad . \quad . \quad (2)$$

$$3Cl + H + 3(HCl) = 21.37 \quad . \quad . \quad (3)$$

$$4Cl = 26.44 \quad . \quad . \quad (4)$$

Now we can calculate

$$H = 1.65 \quad . \quad . \quad (1)$$

$$Cl = 6.61 \quad . \quad . \quad (4)$$

from (2) we obtain

$$4(HCl) = -0.14$$

from (3)

$$3(HCl) = -0.11$$

So

$$(HCl) = -0.04.$$

The values found for X are: H = 1.65, F = 1.71, Cl = 6.61, Br = 9.75 and I = 16.29, which are in good agreement with the boiling-point theory.⁷ The resulting mutual actions are to be found in Table II.

⁶ St. Friberg, *Z. Physik*, 1927, 41, 378.

⁷ J. M. Stevels, *Chem. Weekbl.*, 1937, 34, 334.

This table seems to have no regularity, but we must not forget that as standard value for X_n we have all through taken the value of the re-

TABLE II.

	H.	F.	Cl.	Br.	I.
H	—	+ 0.16	— 0.04	— 0.23	— 0.73
F	+ 0.16	—	+ 0.02	— 0.28	— 0.60
Cl	— 0.04	+ 0.02	—	— 0.10	— 0.39
Br	— 0.23	— 0.28	— 0.10	—	?
I	— 0.73	— 0.60	— 0.39	?	—

fracture. For purpose

of comparison we need a certain norm, for which the following may serve.

The meaning of $(X_n X_m)$ is $\Delta_{X_n}^{X_m} + \Delta_{X_m}^{X_n}$.

We know from the above, that $\Delta_{X_n}^{X_m}$ represents the change which the refraction of the ion X_n undergoes under the influence of the ion X_m , in comparison with its state in the compound CX_{n4} . Take now the compound $CX_n^{(1)} X_n^{(2)} X_n^{(3)} X_n^{(4)}$ and consider the ion $X_n^{(1)}$; if we now replace $X_n^{(4)}$ by X_m the mere removal of $X_n^{(4)}$ causes the field of the central C ion to be less counteracted and ion $X_n^{(1)}$ comes into a stronger field, the refraction of $X_n^{(1)}$ decreases to an extent given by

$$\Delta_{X_n^{(1)}} = - C_{X_n^{(4)}} \frac{[R_{X_n^{(1)}}^2]}{r_{X_n^{(1)}}^4}.$$

This can be seen in the following way: if we suppose (a) that an ion $X_n^{(1)}$ is caught in the field of the configuration $\begin{smallmatrix} X_n^{(3)} \\ -C- \\ X_n^{(2)} \end{smallmatrix}$ from the hypothetical free state, and (b) that the field of the C^{++++} ion is predominant, we have, according to Fajans⁸

$$\Delta[R_1] = - C \frac{[R_{X_n^{(1)}}^2]}{r_{X_n^{(1)}}^4},$$

where $\Delta[R_1]$ represents the decrease of the refraction of the ion $X_n^{(1)}$, due to (a) above, $[R_{X_n^{(1)}}]$ represents the refraction of the ion $X_n^{(1)}$ and $r_{X_n^{(1)}}^{(1)}$ represents the distance from the central ion to the halogen or hydrogen ion $X_n^{(1)}$. Now, $r_{X_n^{(1)}}^{(1)}$ is proportional to the radius of the latter ion, since we must assume that in methane derivatives there is anion-anion contact.⁹

Consider now the case in which the ion $X_n^{(1)}$ is caught in the field of the conjugation $\begin{smallmatrix} X_n^{(3)} \\ X_n^{(4)}C- \\ X_n^{(2)} \end{smallmatrix}$. In this case the decrease is less, because the field

⁸ K. Fajans, *Z. physik. Chem., A*, 1927, 130, 724.

⁹ Discussed *in extenso* elsewhere, J. M. Stevels, *Chem. Weekbl.*, 1937, 34, 334.

is counteracted by the presence of $X_n^{(4)}$; this influence can be described by an additional factor to C , so that the decrease is now

$$\Delta[R_2] = - \left(C - C_{X_n^{(4)}} \right) \frac{R_{X_n^{(1)}}^2}{r_{X_n^{(1)}}},$$

and we find

$$(\Delta X_n)_1 = \Delta[R_1] - \Delta[R_2] = - C_{X_n^{(4)}} \frac{R_{X_n^{(1)}}^2}{r_{X_n^{(1)}}^4}.$$

It must be noted that Fajans proposed his formula for the decrease of the refraction in the halogen ions only for the halides of alkaline metals. Here we modify the formula with another constant C . This suggestion seems to fit very well with the measured mutual actions.

TABLE IV.

	$-\beta \times 10^4$	A
H	100	30
F	63	6
Cl	60	36
Br	8	56
I	0	101

	Emp.	Theor.
(HF)	+ 0.16	+ 0.09
(HCl)	- 0.04	- 0.02
(HBr)	- 0.23	- 0.24
(HI)	- 0.73	- 0.71
(FCl)	+ 0.02	- 0.01
(FBr)	- 0.28	- 0.28
(FI)	- 0.60	- 0.60
(ClBr)	- 0.10	- 0.10
(ClI)	- 0.39	- 0.39

$C_{X_n^{(4)}}$ is a constant which shows the "influence" of the ion $X_n^{(4)}$ and will clearly be greater the more the ion counteracts the field. We shall omit the indices (1), (4), as a simplification. Now for halogens in methane derivatives¹⁰

$$[R_{X_n}] \sim r_{X_n}^5,$$

so that we may write

$$(\Delta X_n)_1 = - \beta_{X_n^{(4)}} r_{X_n}^6.$$

$(\Delta X_n)_1$, thus, is the decrease of the refraction of the ion $X_n^{(1)}$ by removing the ion $X_n^{(4)}$. If we now introduce the ion X_m , the field of the central ion is more counteracted, the refraction of X_n again increases by $(\Delta X_n)_2 = + \beta_{X_m} r_{X_n}^6$ and the total change in its refraction due to the replacement of $X_n^{(4)}$ by X_m is therefore

$$\Delta X_n^m = (\Delta X_n)_1 + (\Delta X_n)_2 = (\beta_{X_m} - \beta_{X_n^{(4)}}) r_{X_n}^6.$$

We now replace $r_{X_n}^6$ by A_{X_n} and find for

$$\begin{aligned} (X_n X_m) &= \Delta X_n^m + \Delta X_m^n = (\beta_{X_m} - \beta_{X_n}) A_{X_n} + (\beta_{X_n} - \beta_{X_m}) A_{X_m} \\ &= (\beta_{X_m} - \beta_{X_n})(A_{X_n} - A_{X_m}), \end{aligned}$$

whence, for $X_n = X_m$, is $(X_n X_n) = 0$. As now the A_{X_n} values are known we can calculate the β values from our $(X_n X_m)$ values.

¹⁰ A. E. v. Arkel and W. de Groot, *Physica*, 1932, 12, 211.

We shall treat the A_H value for the moment as unknown, since as $[R_H]$ is not proportional to r_H^5 , the latter being not exactly known. As we use the A values only in comparison with each other, it is permissible to use for r_x the ionic radii given by Pauling.⁹

We now assume $\beta_I = 0$, because we always determine differences. We have now nine equations for the five unknown values β_H , β_F , β_{Cl} , β_{Br} and A_H , which can now be calculated; the results are given in Table III. From these figures all the mutual actions can be calculated (Table IV.). The agreement may be considered good as an error of ± 0.03 can be expected.⁵ The refraction from the liquid compounds CX_1 , X_2 , X_3 , X_4 can therefore, generally speaking, be represented by

$$[R] = \sum_{n=1}^4 X_n + \frac{1}{2} \sum_{n,m} (\beta_n - \beta_m)(A_m - A_n).$$

We can now calculate what change of refraction an ion undergoes from the presence of other ions. ΔX_n^m can be calculated now

$$\Delta X_n^m = (\beta_{X_m} - \beta_{X_n})A_n.$$

The results are given in Table V.

In the first place we see that the refraction of a particular ion is more and more increased when the central ion carries other larger ions. At first sight this is quite unexpected.

If we regard the bound ions as non-polarised negatively charged spheres, the larger these ions become, the less counteracted will be the field of the central ion, the greater the energy of the bond and the less refraction of the ion in question.

TABLE V.

by Change of	H(Δ_H).	F(Δ_F).	Cl(Δ_{Cl}).	Br(Δ_{Br}).	I(Δ_I).
H(Δ_H)	0	+ 0.11	+ 0.12	+ 0.28	+ 0.30
F(Δ_F)	- 0.02	0	0	+ 0.03	+ 0.03
Cl(Δ_{Cl})	- 0.14	- 0.01	0	+ 0.19	+ 0.21
Br(Δ_{Br})	- 0.52	- 0.31	- 0.29	0	+ 0.04
I(Δ_I)	- 1.01	- 0.63	- 0.60	- 0.08	0

Van Arkel and de Boer¹¹ previously calculated for methane and ethane derivatives (assuming a constant atomic refraction for the halogens), that hydrogen ions will have a higher refraction when they occur in a greater amount; these authors gave a similar explanation, *viz.*, that

the more the field of the central ion is counteracted by small ions (*i.e.* hydrogen ions) the greater will be the refraction of the ions in question. These authors considered only the chlorine derivatives of the methane series. The present results show, however, an exactly opposite tendency. In the chlorine series we find for the refraction per ion (Table VI.).

The figures themselves are of course some what inexact, but their trend is significant. According to Van Arkel and de Boer¹¹ the refraction of hydrogen decreases from CH_4 towards $CHCl_3$. A similar trend to that given in Table VI. is found in the series $CH_4 \rightarrow CBr_4$ and $CH_4 \rightarrow CCl_4$. A description which takes into consideration the Coulomb forces only is thus

TABLE VI.

	Refr. H.	Refr. Cl.
CH_4	1.65	—
CH_3Cl	1.77	6.19
CH_2Cl_2	1.89	6.33
$CHCl_3$	2.01	6.47
CCl_4	—	6.61

¹¹ A. E. v. Arkel and J. H. de Boer, *Z. physik. Chem.*, A, 1926, 122, 101.

certainly not permissible; we must take several effects into consideration. We are concerned only with the liquid state and therefore the surrounding molecules will exercise an influence upon a particular ion X; halogen ions in the surrounding molecules increasing in size will diminish the field in that ion. If the first-mentioned halogen ions are smaller many more lines of force will run through the ion X. The refraction will be hereby increased. Assuming only Coulomb forces, with an increase of the radius of the other substituents of the methane derivative, the refraction of a particular ion X will decrease in consequence of the action of the ions of the same molecule and increase in consequence of the action of the ions of other molecules. It is an obvious assumption that the first influence is far stronger than the latter. The total effect, therefore, is that in consequence of the Coulomb action the refraction of the ion X decreases as the radius of the other substituents increases. This is not in agreement with our values, but we must not forget that the larger the halogen ions are, the more they can be polarised. The induced dipole will counteract the central ion. This effect increases as we pass to larger halogen ions and the refraction of the ion X will therefore be increased. From the ions of other molecules a dipole effect may also be expected, *viz.*, a decrease of the refraction of ion X, but this will be negligible in comparison with the first dipole effect, since we must assume that the induced dipole is localised between the centre of the halogen ion and the centre of the C ion. The total effect of the dipole action as the substituents increase in size, is, thus an increase of the refraction of the ion X in question.

Thus we have two effects which counteract one another; the Coulomb action will cause the refraction of X to decrease, while the dipole action will cause the refraction of X to increase, if we change the other substituents successively from F to I. We may call the behaviour of the refraction due to the Coulomb forces "normal." If we examine a particular halogen ion X and replace the other substituents gradually by larger ones, the refraction of X will first decrease, but, finally, the dipole effect will cause it to increase once more. There should, therefore, be minimum value, but from our figures we can deduce that this effect would be reached in the carbon derivatives only for hypothetical halogen ions smaller than hydrogen. The "normal" or "preponderantly Coulomb" behaviour of the refraction is not realised in the carbon derivatives. The refraction is abnormal and principally determined by the polarisation effect. This abnormal behaviour is thus expressed in the increase of the $\Delta_{X_n}^{X_m}$ values of $\Delta_{X_n}^H$ as we pass to $\Delta_{X_n}^I$, or, as is essentially the same thing, the increase of β_H to β_I .

We now assume that the course of the refraction in the gaseous state is quite the same as in the liquid state; this is permissible, as was shown above, since the refraction of the liquid and the gaseous state do not differ materially.

We have now found a method for estimating the contribution of each individual halogen ion to the refraction, and therefore (on the basis of Fajans and Joos's hypothesis) the direction in which the strength of the electrostatic field changes, or (according to Wolf and Herzfeld), the extent to which the energy of the bond is modified. In other words in what sense the energy is modified by progression in a particular series.

Clearly this must be connected with the restoring force constant of the vibration which corresponds to the valency bond and also with the energy of activation that is required for the reaction with sodium vapour which will break up this bond.

Polanyi and co-workers generally give the collision number of the reaction. From the above it can be seen that a decrease of restoring force

constant and collision number accompanies an increase of refraction. Polanyi and Ogg² lay special stress upon the first two factors.

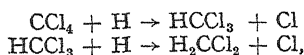
We will first consider the halogens in the methane derivatives. In the series CH_3X , according to the most recent calculations by Heller and Polanyi¹ we find (Table VII.).

Unfortunately, there are not sufficient data known for the series CH_2X_2 , CHX_3 , and CX_4 to serve for comparison. Table VIII. contains figures for the methane derivatives so far known.

We should here again emphasise that too much importance must not be attached to the values for the refraction, which involve too many hypothetical elements, but the trend clearly indicates the anticipated change

with the restoring force constant and the collision number.

There is also a striking correspondence between our theory and the experiment of Cremer, Curry and Polanyi,¹² on the reactions of various methane derivatives to hydrogen atoms, *e.g.*,



and similar reactions. They conclude that the reaction velocity increases from CH_3Cl to CCl_4 . The striking thing is that the reactivity of the hydrogen in the methane derivative is also increased when more chlorine ions are introduced (H_2 as well as HCl is generated in a greater amount). It seems as if in this case the molecule becomes more and more weakly bound.

This behaviour can be foreseen on the basis of our refraction data. It has been shown that in the series $\text{CH}_3\text{Cl} \rightarrow \text{CCl}_4$, the refraction values for both hydrogen and halogen in-

TABLE VIII.

	Coll. Number.	Rest. Force Constant.	Refr. X.
CH_3Cl	7100	3.12	6.19
CH_2Cl_2	310	2.94	6.33
CHCl_3	22	2.47	6.47
CCl_4	2	2.00	6.61
CH_3Br	75	2.61	8.19
CH_2Br_2	—	2.56	8.71
CHBr_3	—	1.82	9.23
CBr_4	—	1.41	9.75
CH_3I	1	2.15	13.26
CH_2I_2	—	2.09	14.27

Table VI. Moreover, these authors, in agreement with Chadwell and Titani¹³ find that the reactivity of the hydrogen ions in the series $\text{CH}_3\text{F} \rightarrow \text{CH}_3\text{I}$ increases. This also is in accordance with our refraction values, as is shown in Table IX.

TABLE VII.

	Coll. Number.	Rest. Force Constant.	Refr. X.
CH_3F	10 ⁶	—	1.65
CH_3Cl	7100	3.12	6.19
CH_3Br	75	2.61	8.19
CH_3I	1	2.15	13.26

TABLE IX.

	Refr. H.
CH_3F	1.76
CH_3Cl	1.77
CH_3Br	1.93
CH_3I	1.95

crease, in other words both the hydrogen and chlorine ions will be more weakly bound, as appears from

¹² E. Cremer, J. Curry, and M. Polanyi, *Z. physik. Chem., B*, 1933, **23**, 445.

¹³ H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, 1933, **55**, 1363.

It is clear that refraction research throws valuable light upon the reactivity of hydrogen and halogen ions in organic compounds. Unfortunately, the experimental material on this subject is extremely small, but an interesting field of research lies open to those who will pursue it.

Summary.

According to Fajans and Joos the refraction is a measure for the electric field, in which a certain ion lies, or, according to Wolf and Herzfeld, for the energy of the bond. Using the empirical formula of Fajans for the decrease of the refraction of an anion, we seek to apply these considerations to the halogenated methane derivatives.

In this way we can foresee the course of the reactivity of hydrogen and halogen ions in organic compounds, as was found by Polanyi and co-workers.

The values found also serve to explain the deviations of the calculated boiling-points of the methane derivatives according to van Arkel and de Boer and give an insight into the regularities, which are found in the dipole moments of almost all halogenated aliphatic compounds. These two questions, however, are not treated here, but will be discussed in detail elsewhere.

Finally, the author wishes to express his heartiest thanks to Professor Dr. A. E. van Arkel for his keen interest in him and his work.

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SYSTEMATICS OF BAND-SPECTRAL CONSTANTS.

PART I.—CALCULATION OF FUNDAMENTAL VIBRATION FREQUENCIES OF NON-HYDRIDE DI-ATOMS (XY TYPE) OF SYMMETRICAL MOLECULAR GROUPS.

By C. H. DOUGLAS CLARK.

Received 9th August, 1937.

The measure of success attained in calculating band-spectral constants by empirical relations appears to encourage further work in the field. It will be remembered that the early study of line-spectra owed much to the previous discovery of such relations. The molecular constants are found to have periodic relationships, akin to those of atoms, a fact to which insufficient attention appears to have been paid up to the present. It is the purpose of the present and succeeding papers to discuss existing and to suggest new relations, due attention being paid to the natural classification of molecules into periods and groups.¹ The methods will be applied to the prediction of undetermined constants wherever possible.

It is hoped that the present method of approaching the problem of spectroscopic constants may prove useful, in encouraging experimental and theoretical developments. From the practical standpoint, some incentive may be given to the task of verification or otherwise of pre-

¹ C. H. Douglas Clark, *Trans. Faraday Soc.*, 1935, **31**, 1017.

dicted numbers, whilst at the same time attention is directed to cases which will probably most amply repay further study. The present work is indeed largely held up by paucity of data, and considerable discretion must be used regarding all proposals where the experimental results are insufficient or unreliable. On the theoretical side, progress by the powerful methods of quantum mechanics has been retarded by difficulties of calculation, and empirical methods may therefore be useful. Some of the results already obtained would appear to provide "question-marks" for the theoretical physicist.

Fundamental vibration frequencies of di-atoms of symmetrical groups form the subject of Parts I., II. and III.

Suggested Relationships between the Ground State Vibrational Frequencies of Di-atoms of Symmetrical Groups.

Various attempts have been made to find a suitable relation between the quantities $a = (\omega_e)_{XY}$, $b = (\omega_e)_{XX}$ and $c = (\omega_e)_{YY}$, where a , b , c are the ground state vibrational frequencies of di-atoms XY, XX, YY respectively, the limitation being imposed that the di-atoms shall belong to *symmetrical* molecular groups, that is, such that X and Y belong to the same Periodic Group and contribute the same number of "valency" electrons to the shared group of XY. The symmetrical groups are those numbered II., IV.s, VI.s, VIII.s, X.s, XII.s and XIV.¹ In such cases, the "Rule of Means"^{1, 2, 3}

$$a = 0.500 (b + c) \quad . \quad . \quad . \quad . \quad (1)$$

s often suitable, but since the errors in a are found to be always positive, the following "Modified Rule of Means" has been suggested:—

$$a = 0.491 (b + c) \quad . \quad . \quad . \quad . \quad (2)$$

Since, however, considerable errors remained in certain cases, attempts were made to satisfy a relation of the type $a = b^n c^p$, where $n + p = 1$. It was assumed that $c > b$, and that the higher frequency c may have greater influence than the lower frequency b in determining the value of a . If we take the two di-atoms ICl and IBr, for each of which a , b and c are known with considerable accuracy, we have two equations, from which $p = 0.653$, $n = 0.338$, so that $n + p = 0.991$, or nearly 1, so that dimensional requirements are satisfied. If now we substitute $p = 0.653$ in the corresponding equations for KNa and SO, we find $n = 0.332$ and 0.336 respectively, so that no great error appears to be involved in taking $n = \frac{1}{3}$, $p = \frac{2}{3}$, giving $a^3 = bc^2$. This relation proved better than earlier attempts, but gave small positive errors, and so became amended to²

$$a^3 = 0.815 bc^2 \quad . \quad . \quad . \quad . \quad (3)$$

In order to test these relationships, frequencies are taken in wave-numbers per cm. (unit: cm.⁻¹).

The equations (1), (2), (3) are now checked against experiment, omitting ICl and IBr, as in Table I. below.

The lowest deviations from experiment occur with a formula of the type (3). If the more doubtful experimental numbers are excluded in taking the mean, the mean error using (3) falls to 1.3 per cent., whilst

² C. H. Douglas Clark, *Nature*, 1937, 139, 508.

³ H. G. Howell, *ibid.*, 1936, 138, 36, 290.

the errors of equations (1) and (2) are not greatly affected. The experimental numbers marked H in Table I. refer to measurements on band-heads, and may not be very accurate. The numbers are taken from well-known books by Jevons⁴ and Sponer,⁵ except in the cases of SeO and TeO.⁶

It is noteworthy that the three formulæ give large positive errors in the cases of PN and AsN. It was suggested by Howell,³ however, that the experimental values of PN (1337.2) and of AsN (1068 cm.⁻¹) might not refer to their ground states. Experiments in absorption would decide this point.

TABLE I.

Di-atom.	Group.	b.	c.	Values of <i>a</i> .			Percentage Errors.			
				Expt.	Calc.			(1).	(2).	(3).
					(1).	(2).	(3).			
KLi . RbLi CsLi KNa RbNa CsNa CsRb	II.	92.6H 57.8H 42.0H 92.6H 57.8H 42.0H 42.0H	351.4 351.4 351.4 159.2H 159.2H 159.2H 57.8H	(207) (185) (170) 123.3H (107) (98) 49.4H	220.0 204.6 196.7 125.9 108.5 100.6 49.9	218.0 200.9 193.2 123.6 106.5 98.8 49.0	210.5 179.8 161.7 124.2 106.1 95.4 48.5	+ 7.25 + 5.31 + 1.60 + 10.60 + 8.59 - 2.70 + 15.71 + 13.65 - 4.88 + 2.11 + 0.24 + 0.72 + 1.40 - 0.47 - 0.85 + 2.65 + 0.82 - 2.65 + 1.01 - 0.81 - 1.82		
BiSb	X.s	172.7H	260.0H	220	220.3	216.4	216.2	+ 0.14 - 1.68 - 1.77		
SO . SeO . TeO .	XII.s	727.4H 387.8H 250.9	1580.3 1580.3 1580.3	1123.7 908.9 796.1	1153.8 984.0 915.6	1133.0 966.2 899.0	1139.8 924.2 799.4	+ 2.68 + 0.83 + 1.44 + 8.13 + 6.17 + 1.56 + 15.10 + 12.90 + 0.40		
BrCl	XIV.	323.9	564.9H	(430)	444.4	436.4	438.4	+ 3.35 + 1.49 + 1.95		
Mean Percentage Errors, neglecting sign.								5.8	4.4	1.9
Ditto, excluding bracketed experimental cases								4.9	3.8	1.3

Some Estimated Frequencies.

It becomes possible to predict the fundamental vibration frequencies of a number of di-atoms, as in Table II. PN and AsN are provisionally included in the Table (see discussion below).

Tables I. and II. show that equations (2) and (3) tend to give similar results for *a* in a given group for smaller values of the difference *c*—*b*, whilst the deviations increase as *c*—*b* increases, that is, as the polar opposition of the atoms X and Y increases. Thus *a*(2) — *a*(3) = — 6.8, 42, 99.6 for SO, SeO, TeO respectively (Table I.), and similar considerations apply in other cases. The *c*/*b* ratio is also important (Part II.). Since *a*(3) for TeO agrees with experiment, whilst *a*(2) departs widely, it appears that in (3) the influence of polar opposition, noticeable in equations (1) and (2), is overcome. The same appears true of SeO and RbLi.

⁴ W. Jevons, *Report on Band-Spectra of Diatomic Molecules* (Appendix II.), Camb. Univ. Press, 1932.

⁵ H. Sponer, *Molekulspektren*. Julius Springer, Berlin, 1935.

⁶ C. S. Piau, *Compt. Rend.*, 1935, 201, 1181.

The values of $a(2) - a(3)$ are 17.2, 118.4, 222, 272 for PN, AsN, SbN, BiN respectively. PN is the only recorded case where the difference $a(2) - a(3)$ is small, but where the calculated values differ from the experimental. This may possibly strengthen the suspicion that the

TABLE II.

Di-atom.	Group.	b.	c.	a (calc.).		
				(1).	(2).	(3).
NaLi .	II.	159.2H	351.4	255.3	250.7	252.1
RbK .		57.8H	92.6H	75.2	73.8	73.9
CsK .		42.0H	92.6H	67.3	66.1	66.4
PbC .	VIII.s	(420)	1641.6	1030.8	1012	972.4
PN .	X.s	780.4	2360	1570.2	1541.9	1524.7
AsN .		432.1H	2360	1396.1	1371.0	1252.0
SbN .		268H	2360	1314.0	1290	1068
BiN .		172.7H	2360	1216.3	1194	922.0
AsP .		432.1H	780.4H	606.3	595.4	598.5
SbP .		268H	780.4H	524.2	514.7	510.4
BiP .		172.7H	780.4H	476.5	468.0	441.0
SbAs .		268H	432.1H	350.1	343.8	344.0
BiAs .		172.7H	432.1H	302.4	297.0	297.3
SeS .	XII.s	387.8H	727.4H	557.6	547.6	550.9
TeS .		250.9	727.4H	489.1	480.3	476.4
TeSe .		250.9	387.8H	319.3	313.6	313.3

assigned fundamental frequency of PN (and AsN) is too small. It has been shown that the X.s group, to which these di-atoms belong, is marked by maximum frequency in any given molecular period (e.g., KK, KL, KM, etc.).⁷ It remains to be seen whether the deviations are to be accounted for by the distinctive characteristics of the group, or whether they may be attributed to uncertainty in the assignment of the ground state frequencies of PN and AsN.

TABLE III.

Di-atom.	Group.	b.	c.	a (calc.).		
				(1).	(2).	(3).
ClF .	XIV.	564.9	1080	822.5	807.7	812.7
BrF .		323.9	1080	701.9	689.3	675.2
IF .		214.3	1080	647.1	635.5	588.4

The fundamental frequency of FF has not been determined with certainty, but it seems very probable from many points of view that the earlier estimate⁸ of 1080 lies near the truth. If this may be accepted, further estimates are as in Table III.

⁷ C. H. Douglas Clark, *Proc. Leeds Phil. Soc.*, 1935, 3, 26.

⁸ *Idem. Trans. Faraday Soc.*, 1935, 31, 585.

An attempt made to apply the formulæ to excited states of molecules failed on account of insufficiency of data, and it is not yet certain whether relation (3) will apply to corresponding excited state frequencies of di-atoms of the specified type.

It becomes clear from the foregoing that the principle of additivity of vibration frequencies, as expressed in the Rule of Means, becomes less applicable the more the bond between X and Y approaches the polar type. The limitation of additivity to covalent links has also been found by Pauling, in respect of bonding energies⁹ and internuclear distances.¹⁰

The author desires to thank Dr. J. Colvin for kind assistance and advice, and Mr. C. W. Scaife, who gave help in calculation.

Summary.

The validity of a relation $a^3 = 0.815 bc^2$, connecting the fundamental vibration frequencies a, b, c of di-atoms XY, XX, YY respectively of symmetrical molecular groups, where $c > b$, has been examined. The relation is found to give generally better results than formulæ of the arithmetic mean type, which appear to be limited to cases where c and b do not differ too greatly, that is, where the polar opposition between X and Y is not very great. It appears that the proposed formula overcomes the influence of polar difference. A number of predicted frequencies are recorded.

⁹ L. Pauling *Jour. Amer. Chem. Soc.*, 1932, **54**, 3570.

¹⁰ *Idem. Proc. Nat. Acad. Sci.*, 1932, **18**, 293.

PART II.—INTERRELATION OF FUNDAMENTAL VIBRATION FREQUENCIES OF SYMMETRICAL DI-ATOMS (XX TYPE) IN THE SAME MOLECULAR GROUPS.

BY C. H. DOUGLAS CLARK AND C. W. SCAIFE.

It has been found in Part I. that an arithmetic mean type of relation $a = \frac{1}{2}(b + c)$ applied to the fundamental frequencies a, b, c of di-atoms XY, XX and YY respectively in the same symmetrical groups is unsatisfactory where the difference of polarity between X and Y is considerable. We may now examine this result, assuming a formula of the pendulum type, whereby we have

$$a = d\sqrt{\frac{k_a}{\mu_{XY}}}; \quad b = d\sqrt{\frac{k_b}{\mu_{XX}}}; \quad c = d\sqrt{\frac{k_c}{\mu_{YY}}};$$

where $d = 1/2\pi$, the k 's denote bond constants (restoring forces per cm. nuclear displacement), and the μ 's reduced masses of the particles concerned. If X, Y represent the masses of the two atoms, and if the bond constants are proportional to the vibration frequencies, so that $k_a = fa, k_b = fb, k_c = fc$, where f is constant for a triad of di-atoms of the specified kind, we have

$$a = d^2 f \frac{(X + Y)}{XY}; \quad b = d^2 f \frac{1}{X}; \quad c = d^2 f \frac{1}{Y};$$

from which the relation $a = \frac{1}{2}(b + c)$ follows. We observe that the arithmetic mean relation depends upon the assumption placed above in

italics, which may be otherwise expressed as $\omega_e \mu = g$, $k \mu = h$, where g , h are constants for the type of diatomic triads in question. Now although bond constants and fundamental frequencies of non-hydride di-atoms have been shown to possess similar periodic character,^{1, 2} proportionality does not hold between them, except approximately when the polar opposition is small. These considerations offer an interpretation of the results.

It seems worth while to illustrate this, and for the purpose we shall consider Group XII.s, where reliable data are available, containing OO, SS, SeSe and TeTe and their intercombinations in pairs. The results of calculation are in Table I., where the bracketed frequency numbers are estimated values taken from Part I.

TABLE I.

Di-atom.	ω_e cm. ⁻¹ .	$\mu (\times 10^{24})$ gr.	$k (\times 10^4)$ dynes/cm.	$e = [\omega_e / k] (\times 10^4)$.	$g = \omega_e \mu (\times 10^{27})$.	$h = k \mu (\times 10^{22})$.
OO .	1584.9	13.19	117.7	13.47	20.90	15.52
SS .	727.4	26.45	49.66	14.64	19.23	13.13
SeSe .	387.8	65.30	34.85	11.13	25.32	22.76
TeTe .	250.9	105.1	23.47	10.69	26.36	24.67
SO .	1123.7	17.60	78.79	14.27	19.78	13.87
SeO .	908.9	21.94	64.31	14.14	19.94	14.11
TeO .	796.1	23.44	52.76	15.09	18.66	12.37
SeS .	(550.9)	37.60	40.52	13.60	20.71	15.24
TeS .	(476.4)	42.23	34.02	14.01	20.12	14.36
TeSe .	(313.3)	80.41	28.01	11.18	25.20	22.53

It is observed that the e values vary considerably, between 10.7 and 15.1. Similar remarks apply to g and h . However, for the triads SO, SS and OO; TeSe, TeTe and SeSe; the constants in a given column do not differ very greatly. Hence, in accordance with theory, the arithmetic mean relation is fairly satisfactory for SO and TeSe, but highly unsatisfactory for TeO, where the e 's are 15.09 (TeO), 10.69 (TeTe) and 13.47 (OO). The experimental results on SO, where the polar opposition is small, and on TeO, where it is large, are in accordance with these views (see Table I. of Part I.). Similar results hold in other symmetrical groups than the one considered (XII.s). The constant e is the reciprocal of f used above.

Howell³ suggested that the bond constants of a triad of di-atoms XX, YY, XY of the specified type should be approximately equal. This is clearly not borne out by the results of Table I., as shown, for example, in the varying k 's of OO, SS and SO.

The results of Part I. show that a cubic relation $a^3 = 0.815bc^2$, where $c > b$, appears to overcome the difficulties inherent in the modified arithmetic mean rule, according to which $a = 0.491(b + c)$. However, in a fairly large number of cases, the two equations give roughly concordant results. If the cubic equation is of the right type, and the arithmetic mean relation faulty for large polar opposition of the constituent atoms in a given case, we may anticipate that they agree only for values of c/b which do not depart too widely from the value unity. The purpose

¹ C. H. Douglas Clark, *Trans. Faraday Soc.*, 1935, **31**, 1017.

² *Idem. Proc. Leeds Phil. Soc.*, 1935, **3**, 26.

³ H. G. Howell, *Nature*, 1936, **138**, 290.

of this paper being to test the applicability of an equation obtained by combining the cubic and mean relations by eliminating a between them, it is important first to examine for what values they give concordant results, or, assuming that the cubic relation may be trusted, over what range both equations give results in agreement with experiment.

If we put $x = c/b$, the relations reduce to $a = 0.491b(x + 1)$ and $a = 0.934bx^{\frac{2}{3}}$; if y is the ratio between these two a values, $y = 0.526(x + 1)/x^{\frac{2}{3}}$. The following then shows corresponding values of x and y :—

x	1	1.5	2	2.5	3	4	5	6
y	1.052	1.003	0.994	0.999	1.012	1.043	1.079	1.115

A graphical representation shows that the curve is nearly parallel to the x axis between $x \approx 1.3$ and 3.0 , and crosses the line $y = 1$ at $x = 1.55$ and 2.60 . Now it happens that (a) no frequency ratios occur less than 1.3 , and (b) the majority of frequencies give ratios between 1.3 and 3.0 , so that it appears that where $c/b < 3$, that is, where the ratio does not depart very far from the value unity, both types of equation give similar and trustworthy results. For values of $c/b > 3$, the effect of polar opposition previously noted comes in, and the cubic relation alone is trustworthy: for example, for SeO ($x = 4.1$), RbLi (6.1) and TeO (6.3), Table I. of Part I. shows that it gives reliable results.

Applicability of a Combination of the Mean and Cubic Relationships.

Eliminating a between the mean and cubic equations, we have

$$0.815bc^2 = 0.491^3(b + c)^3,$$

$$\text{or} \quad c^3 - 3.9c^2b + 3cb^2 + b^3 = 0 \quad (1)$$

Examination of this equation shows that, for a given value of b , the cubic in c has one negative root (neglected) and two positive roots, one of which is 1.68 times the other. The same is true for given values of c , solving for b . Now equation (1) connects the frequencies of symmetrical di-atoms XX of the same group, and may be capable of limited applicability so long as the frequency ratios lie in the region 1.68 . It is found that in a given group the ratios approximate most nearly to this value in the region of lower frequencies (higher molecular weights): thus the ratio of the frequencies of NN to that of PP is 3.02 , PP to AsAs 1.81 , AsAs to SbSb 1.61 , and SbSb to BiBi 1.55 . The frequency ratios in all groups examined approach about the same limiting ratio with increasing molecular weight, so that we may expect the best results with the heavier di-atoms. For example, if we put b for the di-atom II as 214 in (1), the two calculated values of c are 560 and 330 , which do not differ greatly from the fundamental frequencies of ClCl (565) and BrBr (324) respectively. Since $c > b$, inserting b in the equation and solving for c will give higher frequencies than b ; conversely, inserting c and solving for b , lower frequencies than c result. Finally, since the frequency ratios of members of different groups approach the 1.68 ratio most nearly for consecutive higher members of a group, we may expect the calculated values to be best in such cases. This is generally supported by the results, shown in Table II., where the numbers in round brackets are not

identifiable with observed frequencies, and those in square brackets have the corresponding experimental figure placed alongside wherever correlation is possible. The interconversions $\text{Br} \rightleftharpoons \text{II}$, $\text{SeSe} \rightleftharpoons \text{TeTe}$, $\text{SbSb} \rightleftharpoons \text{BiBi}$ appear to be quite well represented, and the same is probably true of $\text{RbRb} \rightleftharpoons \text{CsCs}$, but here possibly the assigned frequency of CsCs is rather high. In illustration of the remark about consecutive members of a group, it will be noted, for example, that whilst TeTe as b gives SeSe as c , it gives a large error for SS . It becomes possible to predict the fundamental frequencies of diatomic eka-caesium as $27\cdot1$ (+), eka-iodine $138\cdot4$, and polonium $157\cdot7$. These predictions appear considerably strengthened by the argument advanced in Part III.

TABLE II.

Di-atom.	Group.	ω_e and Ratios.	$\omega_e = b.$	$\omega_e = c.$
			Values of c (calc.).	Values of b (calc.).
KK RbRb CsCs	II.	93 > 1·60 58 > 1·38 42?	(241) [150] NaNa 159 [109·3] KK 93	(143) [89·5] KK 93 [65] RbRb 58
AsAs SbSb BiBi	X.s	429 > 1·61 270 > 1·55 173	(1117) [703] PP 780 [449·3] AsAs 429	(665) [417·7] AsAs 429 [267·5] SbSb 270
SS SeSe TeTe	XII.s	727 > 1·88 388 > 1·55 251	(1892) (1010) [653] SS 727	(1126) (599·9) [388·3] SeSe 388
ClCl BrBr II	XIV.	565 > 1·7 324 > 1·5 214	(875) FF ? (844) FF ? [560] ClCl 565	(1469) [502] ClCl 565 [330] BrBr 324
				[365] BrBr 324 [209] II 214 [138·4] (eka-I) ₂
				[279·3] TeTe 251 [148·9] PoPo (93·5)
				[217] II 214 [124·6] (eka-I) ₂ (82·3)

The queried fundamental frequency of FF of 844 is probably unreliable, although it happens to agree rather well with a possible value 837 given by Sponer.⁴ It seems much more probable that the value 1080 adopted in Part I. lies nearer the truth.

No very high standard of accuracy can be claimed for equation (1), even in the limited range to which it applies. On the other hand, the scheme probably assigns the fundamental frequencies of eka-iodine and eka-caesium in the right region. In the interpretation of spectra, the alternative frequencies where the ground state of a molecule is uncertain usually lie fairly far apart, and it is here that such and similar estimates may prove valuable. At the moment, our only purpose is to show how far equation (1) actually connects together the frequencies of symmetrical di-atoms in a given group.

Whatever meaning may underlie equation (1), it seems possible that the results may be partly accounted for by the empirical assignments of the constants 0·491 and 0·815 in the mean and cubic equations respectively. The constants may satisfy theoretical requirements hitherto undetermined.

Consideration of the cubic equation (1) shows that the roots c/b are 2·60, 1·55 and -0·25; the two positive roots therefore stand in the

⁴ H. Sponer, *Molekülspektren*, Julius Springer, Berlin, 1935.

ratio $2.60 : 1.55 = 1.68 : 1$, as previously found. It follows that the ratio between the positive roots is always 1.68, whether the equation be solved for b by substituting c , or *vice versa*.

Summary.

A cubic equation $c^3 - 3.9c^2b + 3cb^2 + b^3 = 0$, where $c > b$, is found to relate the ground state frequencies of di-atoms of XX type in the same molecular group in the region of lower frequencies (higher molecular weights). Consideration of the equation leads to prediction of the fundamental frequencies of diatomic eka-caesium, polonium and eka-iodine. Assuming a pendulum type formula for nuclear vibrations, it is shown that an arithmetic mean type of relationship, discussed in Part I., will only apply where bond constants are proportional to vibration frequencies, a condition which does not hold unless the polar opposition between the atoms X and Y of a di-atom XY is small.

PART III.—A SIMPLE MODIFICATION OF MATUYAMA'S RELATION CONNECTING THE GROUND STATE FREQUENCIES OF DI-ATOMS XX IN THE SAME GROUPS.

BY C. H. DOUGLAS CLARK.

Matuyama's Relation.

Matuyama¹ suggested that the logarithms of the ground state vibrational frequencies of symmetrical di-atoms of XX type in the same groups were in linear relationship with the logarithms of the atomic weights of X. It was found, however, that discrepancies occurred in the LL Period, containing NaNa, PP, SS and ClCl. We may write the relation as

$$\log \omega_e + k \cdot \log A = \text{a constant},$$

where k is a constant for a given group, and A is the atomic weight concerned. Since for di-atoms of the type considered the reduced mass μ is equal to $(A/2) \times 1.649 \times 10^{-24}$, we may express the relation as

$$\log \omega_e + l \cdot \log \mu = m \quad (1)$$

with l and m as further constants. Alternatively, the relation is $\omega_e \mu^l = k_1$, which when $l = 1$ reduces to the condition $\omega_e \mu = \text{a constant}$, found in Part II. to be an essential condition underlying the "Rule of Means." We find that l is 1.0055 in the Group from NN to BiBi, so that here the condition is nearly fulfilled; in other groups, the value of l is distinct from and less than 1, so that Matuyama's relation becomes inconsistent with the Rule of Means. This rule having been shown to be unreliable in some cases, equation (1) may well lie near the truth.

Modification of the Above Relation.

It is clear that Matuyama's relation cannot be applied to the interesting cases of eka-caesium and eka-iodine, for which the ω_e 's have

¹ E. Matuyama, *Nature*, 1934, 133, 567.

been estimated in Part II., but for which the μ 's are unknown. We have therefore tested the applicability of the modified expression

$$\log \omega_e + n \cdot \log (2Z) = p \quad (2)$$

where n and p are constants, and $2Z$ is the number of extranuclear electrons of a di-atom XX. This relation is equivalent to $\omega_e Z^n = k_2$. On the whole, this equation is more successful than Matuyama's, although divergences still appear in the LL Period. Since we are here mainly concerned with the heavier di-atoms in higher periods, this exception need not concern us very greatly. The procedure adopted in examining equations (1) and (2) is to evaluate the constants l, m, n, p from two cases in each group (LiLi and CsCs in Group II., NN and SbSb in X.s, OO and TeTe in XII.s, FF and II in XIV.), and proceed to apply these numbers to other members of the group. Results are in Table I., where $\omega_e(3)$ refers to numbers obtained by the method described in Part II., and $\omega_e(1)$ and $\omega_e(2)$ refer to the corresponding equations given above. The unreliable results in the LL Period are placed in brackets.

TABLE I.

Group.	Constants.	Period.	Di-atom.	$\mu (\times 10^{24})$ gr.	$2Z$	$\omega_e(1)$	$\omega_e(2)$	$\omega_e(3)$	ω_e (expt.).
II.	$l = 0.7219$	LL MM NN —	NaNa KK RbRb (eka-Cs) ₂	18.96	22	(148.9)	(136.0)	—	159.2
	$m = 3.0954$			32.15	38	(101.6)	91.2	89.5	92.6
	$n = 0.7305$			70.45	74	57.7	56.1	59.7	57.8
	$p = 3.1142$			—	174	—	30.1 (+)	27.1	—
X.s	$l = 1.0055$	LL MM OO	PP AsAs BiBi	25.58	30	(1059)	(1026)	—	780.4
	$m = 4.441$			61.78	66	436.5	431.5	417.7	432.1
	$n = 1.0955$			172.3	166	155.6	157.4	174.5	172.7
	$p = 4.629$			—	—	—	—	—	—
XII.s	$l = 0.8867$	LL MM —	SS SeSe PoPo	26.45	32	(852.3)	(799.8)	—	727.4
	$m = 4.192$			65.30	68	382.0	380.2	388.3	387.8
	$n = 0.9831$			—	168	—	156.3	157.7	—
	$p = 4.382$			—	—	—	—	—	—
XIV.	$l = 0.8517$	LL MM —	ClCl BrBr (eka-I) ₂	28.86	34	(641.8)	(604.5)	560.0	564.9
	$m = 4.0514$			65.89	70	318.0	312.9	330.0	323.9
	$n = 0.9120$			—	170	—	139.4	138.4	—
	$p = 4.1784$			—	—	—	—	—	—

The average percentage errors using equation (2) are smaller than with equation (1). Moreover, (2) seems to confine the anomalous cases to the LL Period better than (1); thus considerable error comes in for the di-atom KK in the MM Period using (1).

It is very noteworthy that the results of $\omega_e(2)$ and $\omega_e(3)$ are closely alike for diatomic eka-Cs, Po and eka-I. Considering the completely different and independent methods of derivation, it seems probable that considerable weight may be placed on these numbers. If we take the nearest whole numbers to the mean by the two methods, we obtain as the respective ground frequencies of (eka-Cs)₂, PoPo and (eka-I)₂: 29, 157 and 139 wave-numbers. If next equation (1) is used to obtain μ 's and so A 's for the three cases, $A = 222, 217$ and 211 respectively. These numbers fit quite reasonably well in the sequence Bi 209, Po 217, eka-I 211, Rn 222, eka-Cs 222, Ra 226, with increasing atomic number

from $Z = 83$ to 88. This measure of agreement further suggests that the predictions lie in the right region. A better sequence could hardly be expected, especially considering that A is very sensitive to small

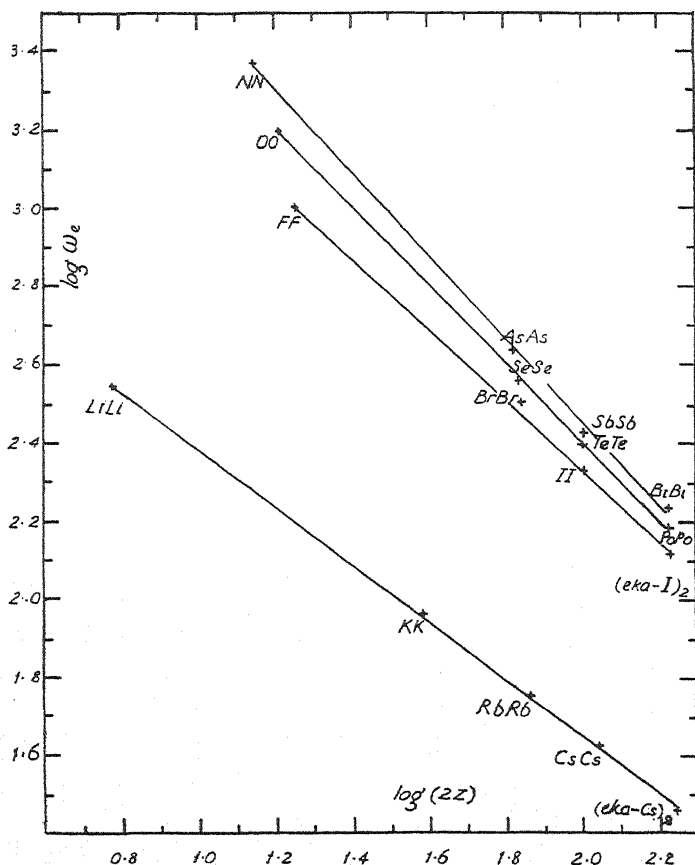


FIG. 1.

changes in ω_e . The linear relationship between $\log \omega_e$ and $\log 2Z$ is shown in Fig. 1, which includes the above predictions, but omits results in the LL Period. It may be noted that the ratio p/n is nearly constant in the four groups of Table I.

Some Estimated Frequencies.

We may now use the equations (1), (2) and (3) of Part I. to obtain estimated fundamental frequencies of di-atoms XY, as in Table II. The results using (3) will be expected to be the most reliable.

It may be noted that the results go some way towards supporting the estimated ground state frequency of FF as 1080 wave-numbers.² It has been shown that this value gives the atomic radius of fluorine in agreement with that from X-ray crystal data, using a modified Morse

TABLE II.

Di-atom.	Group.	<i>b</i> (estd.).	<i>c</i> (expt.).	<i>a</i> (calc.).		
				(1).	(2).	(3).
Eka-CsLi .	II.	29	351·4	190	187	143
Eka-CsNa .		29	159·2	94	92·5	84·5
Eka-CsK .		29	92·6	61	59·5	58·5
Eka-CsRb .		29	57·8	43·5	42·5	43
EkaCsCs .		29	42·0	35·5	35	34·5
PoO .	XII.s	157	1580·3	868·5	853	683·5
PoS .		157	727·4	442	434	407·5
PoSe .		157	387·8	272·5	267·5	268
PoTe .		157	250·9	204	200	200·5
Eka-IF .	XIV.	139	(1080)	609·5	598·5	509·5
Eka-ICl .		139	564·9	352	345·5	330·5
Eka-IBr .		139	324·2	231·5	227·5	228
Eka-II .		139	214·3	176·5	173·5	173·5

function.³ Experiments in absorption would decide this point. The results generally show a satisfactory degree of concordance when independent empirical methods are compared.

The author's thanks are accorded to Dr. J. Colvin for assistance in the preparation of this paper.

Summary.

It is found that the relation $\log \omega_e = p - n \log 2Z$, where *p* and *n* are constants in a given group of symmetrical di-atoms of XX type and *Z* is the atomic number of X, is satisfactory, except in the LL Period. Matuyama has used a similar relation, and found the same limitation, using atomic weight instead of atomic number. The two relations are compared, and it is found that the atomic number equation is rather more satisfactory. The fundamental frequencies of eka-caesium, polonium and eka-iodine are predicted to lie in the respective regions 29, 157 and 139 wave-numbers. The results are shown graphically and found to be in generally good agreement with those from the independent method of Part II. Some further predictions are also made.

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³ C. H. Douglas Clark, *Nature*, 1934, 134, 99.

MULTIPLY STRUCTURE IN A CRYSTALLINE ELECTRIC FIELD OF CUBIC SYMMETRY.

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1. Introduction.

Observation has shown that the spectra of solids are extremely complicated and do not allow the determination of the energy levels from which they arise by any simple means. Thus, for example, the absorption spectra of crystals of hydrated salts of many rare-earth and iron-group elements contain a remarkable number of sharp lines. Recently several observers, notably Spedding and his collaborators,¹ have made a series of accurate measurements of the absorption spectra of a number of these salts. The problem now awaiting solution is to deduce the energy levels of the crystal from these measurements.

Simple experiments, for example the comparison of the spectra of different salts with the same metallic ion, show that the absorption spectrum is that of the metallic ion. Since the absorption is very different from that of the ion in the free state, however, the crystalline forces acting upon the metallic ion must profoundly influence the appearance of its energy spectrum. We may regard each degenerate level of the free ion as decomposed by the crystalline forces into a number of distinct levels. At a temperature T only a few of the ions will occupy levels with an energy interval from the lowest state much greater than kT because of the Boltzmann factor. Consequently, by comparing spectra at different temperatures direct indications are obtained of the existence of any levels lying close to the lowest level. This is the method used by Spedding and his collaborators to obtain the energy diagrams of the simpler rare-earth ions in crystals.

There are two other experimental methods which have been used to determine the position of these low-lying electronic levels of the ion, both involving the measurement of the temperature variation of a property of the crystal at low temperatures. In one method it is the specific heat whose variations are measured, in the other it is some magnetic property such as the paramagnetic susceptibility. To illustrate the former of these, let us suppose that the specific heats of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and the corresponding salt of Nd have been accurately measured over the range 3°K. to room temperature. These two crystals are so similar in structure that any difference in the behaviour of their specific heat curves must be due simply to a difference in the electronic spectra of the metallic ions. Now it is known that Gd^{+++} has a ground state 8S and also that S states are practically uninfluenced by a crystalline electric field which is the most important perturbation of the ion in the crystal. In other words, the specific heat of gadolinium sulphate is entirely due to the lattice vibrations. Hence the difference between the two specific heat curves represents the specific heat of the

¹Spedding and Hamlin, *J. chem. Physics*, 1937, 5, 430, and many papers earlier in the year.

Nd^{+++} ion due to its electronic motion. From the shape of the curve obtained by plotting the differences of the specific heats against temperature it is possible to locate the approximate positions of the few lowest levels.

Ahlberg, Blanchard and Lundberg² have used this method for the salt $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and have definitely found a level at about 80 cm^{-1} above the lowest level. This will be double according to a general theorem of Kramers³ that the energy levels of an ion with an odd number of electrons, such as Nd^{+++} , are at least doubly-degenerate. As the comparison was made at temperatures below 50°K . they were unable to establish directly the existence of a level at 260 cm^{-1} , which was found by Spedding, Hamlin and Nutting,⁴ although such a level would be in good agreement with their results.

The determination of the position of the lowest energy levels of the ion from the temperature variation of the magnetic susceptibility is in principle similar to the determination from the specific heat data. One assumes that the para-magnetic ion is acted upon by a crystalline electric field whose symmetry properties agree with those of the local surroundings of the ion. The mathematical expression for the potential of this field has the same symmetry but still involves a number of arbitrary scale factors. The susceptibility is then evaluated and the scale factors adjusted until agreement with the experimental susceptibilities is obtained. Once again, the method gives with the greatest accuracy one or two levels just above the lowest level.

Penney and Schlapp⁵ have attempted to estimate the character and size of the crystalline field in the salts $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. They find that a fourth order field of cubic symmetry $D(x^4 + y^4 + z^4)$ gives quite good agreement with measurements of the magnetic susceptibility provided the scale factor D is given appropriate values. In the case of Nd^{+++} the ground state $^4I_{9/2}$ is decomposed by this field into three sets of levels at 0 (double), 244 cm^{-1} (quadruple), 810 cm^{-1} (quadruple). Spedding⁴ by direct spectroscopic observation on this crystal has since claimed to have found levels at 0, 77 and 260 cm^{-1} . These levels have the same relative separation, but only one-third of the overall separation of those predicted by Penney and Schlapp, and the conclusion is drawn that the value of D estimated by Penney and Schlapp is three times too large. This new value of D would make the crystalline field for Nd^{+++} very nearly the same as that deduced for Pr^{+++} by magnetic data. As pointed out by Spedding,⁴ the magnetic measurements of Zernicke and James,⁶ and of Selwood,⁷ support the smaller value of D . However, these measurements were not so complete as those of Gorter and de Haas⁸ upon which Penney and Schlapp based their calculations. Bose and Mukherji⁹ have recently found direct evidence of a frequency 249 cm^{-1} in the absorption spectrum of the crystal $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$. In this case the presence of six molecules of water of crystallisation gives strong support to a field of cubic symmetry. Whether the interval is the one 244 cm^{-1} predicted by Penney and

² Ahlberg, Blanchard and Lundberg, *J. chem. Physics*, 1937, **5**, 552.

³ Kramers, *Proc. Amst. Acad.*, 1929, **32**, 1176.

⁴ Spedding, Hamlin and Nutting, *J. chem. Physics*, 1937, **5**, 191.

⁵ Penney and Schlapp, *Physic. Rev.*, 1932, **41**, 201.

⁶ Zernicke and James, *J. Am. chem. Soc.*, 1926, **48**, 2827.

⁷ Selwood, *ibid.*, 1933, **55**, 3161.

⁸ Gorter and de Haas, *Leiden Comm.*, 218b.

⁹ Bose and Mukherji, *Nature*, July, 1937, **140**, 109.

Schlapp, or is the one 250 cm.^{-1} found by Spedding¹⁰ is not clear, but the latter is probably the true explanation.

In the absorption spectrum there may also appear vibrations of the ion and its co-ordinate atoms. Evidence of this is given by experiments of Joos and Bohm¹¹ on chrome alum using both ordinary water and heavy water of crystallisation. They find a shift in the levels of one crystal relative to the other of the order to be expected for a change in the vibration frequencies due to the different mass factors. Possibly some of the levels in the spectra of the hydrated rare-earth sulphates involve coupling of the electronic motion of the ion and the vibrations of the lattice. Indeed, no other explanation seems capable of explaining the extraordinary number of lines in the spectra.¹² However no explicit calculations have yet been made on this point and for the moment it is better to confine ourselves to the simpler case of the pure electronic spectrum of the ion.

To sum up, the assumption of an internal field of cubic symmetry for certain hydrated crystals of rare earth salts promises an important correlation of magnetic susceptibility measurements and direct observations of the absorption spectra. In the following paper we shall therefore obtain the patterns produced by fields of cubic symmetry in all the levels of rare earth ions together with numerical factors for each level that will enable the calculation of the absolute magnitude of the splittings produced by the same crystalline field on different levels.

2. Procedure.

The magnitude of the electric field acting on the rare-earth ions in crystals is small enough not to disrupt seriously the Russell-Saunders coupling of the electrons of the ion, so that the field may be treated as a perturbation upon the ion in its free state. Assuming that the wavefunction of any of the perturbed states may be written

$$\psi = \sum_n a_n \psi_n^0$$

where the summation is over *all* the free states ψ_n^0 of the ion, we derive in the usual way a secular equation of an infinite order. Owing to the size of the electric field, however, it is possible to neglect all elements of the secular determinant involving two states which have not the same set of quantum numbers $l_1, s_1, l_2, s_2, \dots, L, S, J$ (l_1, s_1 being the individual quantum numbers of the first electron of the ion, and so on). The matrix elements which are not negligible have the above quantum numbers equal and differ only in the quantum number M , which, when J is fixed, can have values ranging from $+J$ to $-J$. The determinant now breaks up into a number of factors each of which provides a finite secular equation of order $(2J + 1)$

$$\text{Det} \{H(J, M : J, M') - W\delta(M, M')\} = 0$$

where $H(J, M : J, M')$ is the matrix element of the Hamiltonian of the motion of the perturbed ion, over two states of the free ion which have all quantum numbers equal except M ; and $\delta(M, M')$ is zero unless $M = M'$, when it is unity. If we move the origin of the energy values

¹⁰ Spedding, *J. chem. Physics*, 1937, **5**, 160.

¹¹ Joos and Bohm, *Physik. Z.*, 1935, **36**, 826.

¹² Van Vleck, *J. physic. Chem.*, 1937, **41**, 67.

W to the position of the unperturbed J -level, *i.e.*, in the free state when the value of M does not affect the energy, the secular equation becomes

$$\text{Det}\{V(J, M : J, M') - W\delta(M, M')\} = 0.$$

where V is the term in the Hamiltonian involving the perturbation. The mean of the $(2J + 1)$ values of W is then zero if the potential satisfies Laplace's equation (see § 4). Also the matrix elements are proportional to the strength of the crystalline field and will depend on the particular configuration of the electrons. In a few cases different configurations have equal elements, but in general each configuration must be considered by itself.

The solution of this equation is simplified if many of the elements are zero. For example, if only those elements are not zero which have $(M - M') = 0, \pm 4, \pm 8$, etc., the secular determinant has up to four obvious factors, two of which are the same. Each of the factors is of much lower order than the original equation and is therefore far easier to solve. The solutions give the energy levels of the possible states of the perturbed ion, with which we are concerned. We have solved it in the particular cases, a crystalline field of cubic symmetry, either of the fourth order or of the sixth order or of a relevant combination of the two orders. The relative positions of the levels are the same, to our degree of approximation, for the set of all electronic configurations with the same value of J in the free state and in the same type of electric field. Only the absolute magnitude varies amongst the members of the set.

Although all the patterns formed by the possible configurations of an ion are needed to explain the absorption spectrum obtained in experiments, it is especially interesting to obtain the absolute magnitude of the splitting of the level of least energy, from which all absorption takes place at ordinary temperatures. In the case of rare-earth ions all electrons form closed shells except those in the $4f$ shell. Also by Hund's rule, the lowest state is that of greatest multiplicity and of the largest value of L consistent with this multiplicity. The quantum number J has then a number of values with associated energies, which form a multiplet of terms. If the $4f$ shell is more than half completed the term with the greatest value of J is lowest, otherwise the term with the least value of J is lowest. This rule has only been tested in one case amongst the rare-earths, but there appears to be no reason why it should not hold for them. By means of it we can obtain probable positions of the lowest levels to compare with the spectroscopic evidence.

3. The Crystalline Field.

The crystalline potential acting on an electron of the ion is usually expanded in a Taylor series about the centre of the ion as origin. Thus

$$\Phi = \text{const.} + (Ax^2 + Bxy + \dots + (Cx^4 + Dy^4 + \dots + Gx^2y^2 + \dots + Kx^3y + \dots)) + \dots$$

In this expansion the terms of odd order have been omitted because they affect the energy spectrum only when interactions with other electron configurations of the ion are considered. This effect is presumably negligible. The influence of these terms, however, in breaking down the validity of the selection rules applying to the free ion should be noted.

Any symmetry possessed by the local arrangement of atoms around

the ion must appear in the leading terms of Φ . Unfortunately, this arrangement is not known definitely in the case of the rare earth elements, but we can make reasonable assumptions from a comparison with known crystals of similar chemical structure. Thus if six atoms are arranged octahedrally or eight atoms cubically around the central ion the main term in Φ should be

$$k(x^4 + y^4 + z^4) + h(x^2y^2 + y^2z^2 + z^2x^2) + g(r).$$

By a rearrangement of the terms this expression, which is the fourth order potential of cubic symmetry, may be written

$$D\{x^4 + y^4 + z^4 - 3 + r^4/5 + f(r)\}.$$

Since $D \cdot f(r)$ causes no splitting of the $(2J + 1)$ components of the level J but merely shifts them bodily, we may ignore $f(r)$ completely. We then have a fourth order potential $D(x^4 + y^4 + z^4 - 3r^4/5)$ which very conveniently satisfies Laplace's equation. Similarly, with complete generality as far as its splitting of the J levels is concerned, the second order potential may be taken as $Ax^2 + By^2 - (A + B)z^2$, which also satisfies Laplace's equation. It may of course happen that the principal axes of this potential differ from those of the cubic term.

Thus even if the charge density of the atoms surrounding the ion overlaps the region occupied by the $4f$ electrons, the two above terms may be adapted to satisfy Laplace's equation. This will not be true for non-cubic terms of the fourth order or any terms of higher order.

We shall write V_o for the potential energy of an electron in the most general field of cubic symmetry (O_h symmetry) and expand it as a sum

$$V_C = c_{(4)}C_{(4)} + c_{(6)}C_{(6)} + \dots \quad (1)$$

In the same way for a field of axial symmetry we write

$$V_A = a_{(2)}A_{(2)} + a_{(4)}A_{(4)} + \dots \quad (2)$$

In these identities $r^6A_{(6)}$ and $r^6C_{(6)}$, for example, are homogeneous of degree 6 in x, y, z , and satisfy Laplace's equation. $r^{2n}A_{(2n)}$ involves x and y only in the combination $(x^2 + y^2)$ and has unity for the coefficient of x^{2n} , e.g., $A_{(2)} = (x^2 + y^2 - 2z^2)/r^2$. The cubic terms are defined except for an arbitrary factor. The quantities $a_{(2)}$, $a_{(4)}$ and $c_{(4)}$ have the dimensions of energy. They indicate the magnitude of the electric field and depend upon the particular model under consideration.

The potential energy of an electron in a general rhombic field may be written

$$V_R = \sum_{l, m, n} u_{lmn} x^{2l} y^{2m} z^{2n} - \sum_{k=0}^{\infty} v_k r^{2k} \quad (3)$$

If V_R satisfies Laplace's equation the coefficients u_{lmn} must be consistent with the relations

$$(2l + 1)(2l + 2)u_{l+1, m, n} + (2m + 1)(2m + 2)u_{l, m+1, n} + (2n + 1)(2n + 2)u_{l, m, n+1} - 2k(2k + 1) \frac{k!}{l!m!n!} v_k = 0 \quad (4)$$

where $k = l + m + n + 1$.

These may be often used as recurrence relations. For example, in the cubic terms C_{2k} , $u_{lmn} = u_{lnm} = u_{mnl} = u_{nml} = u_{nlm} = u_{nml}$ and the equations determine the u 's in terms of v_k , except for a simple

scale factor, when $k = 2, 3, 4, 5, 7$. If k has other values, one or more arbitrary ratios appear and the cubic expression breaks into parts. We shall, however, only be concerned with the values $k = 2$ and $k = 3$. For cubic fields v_k is a parameter in the coefficients u_{lmn} only because of our use of four variables x, y, z and r not independent of one another. It will disappear from the expression for $C_{(2k)}$ if we substitute for x, y and z in terms of the spherical co-ordinates r, θ and ϕ , and so reduce the number of variable to three. It may be used to give a desired value to one of the coefficients u_{lmn} ; for example, if $k = 2$ we can choose v_2 so that the x^2y^2 type of term disappears.

In this way we obtain the forms

$$C_{(4)} = (x^4 + y^4 + z^4)/r^4 - 3/5 \quad (5)$$

$$C_{(6)} = \{x^6 + y^6 + z^6 + 15/4(x^4y^2 + x^2y^4 + \dots)\}/r^6 - 15/14 \quad (6)$$

$$= \frac{1}{32}\{5/7 - 15 \cos^2 \theta + 45 \cos^4 \theta - 33 \cos^6 \theta + 3(11 \cos^2 \theta - 1) \sin^4 \theta \cos 4\phi\} \quad (7)$$

Potential due to Six Point Charges Arranged Octahedrally.

—The crystal structure of salts of the type $X_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, where X is a rare earth element, and other salts of these elements which contain a large number of molecules of hydration, is not known but most probably each X atom is surrounded by six oxygen atoms. This view is to some extent supported by the variations of the magnetic susceptibility of such crystals.⁵ As an approximation to the field in this case we may suppose that each oxygen atom has acquired an additional electron, so that the potential energy of an electron at a point (x, y, z) referred to the centre of the ion as origin will be that of an octahedral arrangement of six point charges— e at $(\pm a, 0, 0)$, $(0, \pm a, 0)$, $(0, 0, \pm a)$ i.e., the potential energy of an electron at this point will be

$$V_C = c_{(4)}C_{(4)} + c_{(6)}C_{(6)} + \dots \text{higher order} \quad (8)$$

where
$$c_{(4)} = \frac{35e^2}{4a^5}r^4 \quad \text{and} \quad c_{(6)} = -\frac{21e^2}{2a^7}r^6 \quad (9)$$

In the case of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ the work of Beavers and Lipson¹³ has shown that the oxygen atoms along one of the principal axes belong to sulphate radicals and lie at a rather greater distance from the ion than the other four, which are parts of water molecules. The crystalline arrangement of rare earth sulphates with four molecules of water per ion may be similar. If this is so, and the distances concerned differ appreciably, terms $A_{(2)}$ and $A_{(4)}$ of considerable magnitude will be introduced into the expression for V . However, there are many crystals in which it is probable that the six atoms are on the same footing and for these the deviation from cubic symmetry of the electric field is much less. Crystals likely to be of this type are those with very large amounts of water of crystallisation, and a few in which the six atoms all originate from the acid radical and may not be oxygen atoms. In all cases small non-cubic terms will occur owing to the presence of hydrogen and other atoms, but these are of importance only in higher order approximations.

4. Matrix Elements of the Crystalline Field.

Before dealing specifically with the matrix elements of the cubic field we shall discuss some general theorems.

¹³ Beavers and Lipson, *Proc. Roy. Soc., A*, 1934, **146**, 570.

Tetragonal Symmetry.—Fields of tetragonal symmetry have matrix elements only for $\Delta M = 0, \pm 4, \pm 8, \dots$. This may be proved as follows. Consider a field of tetragonal symmetry of degree $2k$. As usual the potential energy of an electron will be

$$V = \sum_{l, m, n} u_{lmn} z^{2n} (x^{2l} y^{2m} + x^{2m} y^{2l}) \quad (10)$$

where $k = l + m + n$, $l = m + p$, and p is positive. The term associated with u_{lmn} may be written $z^{2n} x^{2m} y^{2m} (x^{2p} + y^{2p})$. Substitute $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, $z = r \cos \theta$. Then z^{2n} does not depend on ϕ , $x^{2m} y^{2m}$ depends only on ϕ through the factor $(\sin \phi \cos \phi)^{2m}$ or its equivalent $(1 - \cos 4\phi)^m$: and $(x^{2p} + y^{2p})$ through the factor $(\cos^{2p} \phi + \sin^{2p} \phi)$ which may be expressed

$$\cos^{2p} \phi + \sin^{2p} \phi = 2^{1-2p} C_p^{2p} \left\{ 1 + \frac{2m(2m-1)}{(m+1)(m+2)} \cos 4\phi + \dots \right\}$$

where the coefficient of $\cos 4\phi$ is $2C_{2s}^m / C_{2s}^{m+2s}$.

Thus ϕ appears in the expansion only as $\cos 4\phi$, $\cos 8\phi$, etc. The matrix elements of V are therefore of the form $\Delta M = 0, \pm 4, \pm 8, \dots$.

The above results hold for fields of cubic symmetry as a special case. Another special case is of importance, namely, that in which the field expression only contains x and y in the combination

$$(x^2 + y^2) = r^2 \sin^2 \theta,$$

that is, it has axial symmetry. As ϕ is not involved in this combination, such a field will only have matrix elements diagonal in M .

It is interesting to note that the terms independent of ϕ in the expansion of $A_{(2k)}$ and $C_{(2k)}$ in powers of $\cos \theta$ are the same and that therefore the diagonal matrix elements of $A_{(2k)}$ and $C_{(2k)}$ are identical. This can be proved by taking the time average of a cubic field $C_{(2k)}$ rotating uniformly about the z -axis. The terms in ϕ will drop out and the resulting field has axial symmetry and contains only terms of order $2k$. It is therefore $A_{(2k)}$.

Complementary Configurations.—Two atoms have complementary configurations when their configurations, apart from closed shells, add up to a closed shell. For example, Ce^{+++} and Yb^{+++} are complementary since the former has a single f -electron and the latter 13 f -electrons. A well-known result in atomic spectra is that to each multiplet of a given configuration there is a corresponding multiplet of the complementary configuration, the two multiplets being inverted with respect to one another. This inversion property still persists when a crystalline field satisfying Laplace's equation removes part or all of the degeneracy of the individual J -levels. We need only prove this for a potential energy $V_{(k)}$ of order k , as a general potential energy can always be expanded as a power series in x , y , and z .

The proof depends essentially on the fact that a potential $V_{(k)}$ satisfying Laplace's equation does not change the mean position of the levels of a given value of J . This mean is given by the spur relation

$$\begin{aligned} (2J+1)\bar{W} &= \sum_M \int |\psi_{JM}|^2 V_{(k)} dv \\ &= \int V_{(k)} \sum_M |\psi_{JM}|^2 dv \\ &= (2J+1) \iiint V_{(k)} \{f(r)\}^2 r^2 \sin \theta d\theta d\phi dr \quad (11) \end{aligned}$$

where there are n electrons, all equivalent, the normalised radial part of the wave-function of each being $f(r)$. The integration over θ and ϕ gives an average value over the surface of a sphere with the origin as centre, and this is zero, *i.e.*, $\bar{W} = 0$.

To such a configuration we can apply the spur relations⁵

$$\sum_J V_{(k)}(J, M : J, M) = \sum_{M_L} V_{(k)}(L, S ; M_L, M_S : L, S ; M_L M_S) \quad (12)$$

where $M = M_L + M_S$, and

$$\begin{aligned} \sum_{L, S} V_{(k)}(L, S ; M_L, M_S : L, S ; M_L M_S) \\ = \sum_i \sum_{m_{l_i} m_{s_i}} V_{(k)}^i(m_{l_i} ; m_{s_i} : m_{l_i}, m_{s_i}) \end{aligned} \quad (12a)$$

where $V_{(k)} = \sum_{i=1}^n V_{(k)}^i$ and $V_{(k)}^i$ is the potential energy of the i th electron in a potential of order k . In addition, m_{l_i} , m_{s_i} take all possible values consistent with $\sum_{i=1}^n m_{l_i} = M_L$, $\sum_{i=1}^n m_{s_i} = M_S$ and the exclusion principle.

Let us consider two such configurations with n and n' electrons respectively, where $(n + n')$ electrons add up to a closed shell. If the systems have the same value of M_L and M_S then to each of the sets of values of m_{l_i} and m_{s_i} obeying the above conditions for one configuration, there is a corresponding set for the other configuration, such that all values of m_{l_i} occur twice in the two sets taken together. Consequently, if we apply (12a) to these two configurations and add the resulting equations, the right-hand side will vanish on account of (11) and therefore

$$\begin{aligned} \sum_{L, S} V_{(k)}(L, S ; M_L, M_S : L, S ; M_L M_S) \\ + \sum_{L', S'} V_{(k)}(L', S' ; M_L, M_S : L', S' ; M_L, M_S) = 0. \end{aligned}$$

Now $V_{(k)}(L, S ; M_L, M_S ; L, S ; M_L, M_S) = F(L, M_L) \epsilon_{L, S}^n$ where $F(L, M_L)$ is a function of L and M_L whose form depends on the potential energy, and $\epsilon_{L, S}^n$ is independent of M_L . Substituting this in the above equation we find

$$\sum_{L, S} \epsilon_{L, S}^n F(L, M_L) + \sum_{L', S'} \epsilon_{L', S'}^{n'} F(L', M_L) = 0.$$

Because the two configurations are complementary, for a given value of M_L and M_S these two summations will involve the same values of L and S , although the factors $\epsilon_{L, S}^n$ may differ. Thus, giving M_L its maximum value for the ground state L_G each summation reduces to a single term and we find

$$\epsilon_{L_G S_G}^n + \epsilon_{L_G S_G}^{n'} = 0.$$

By giving M_L other values we successively find that $\epsilon_{L S}^n = -\epsilon_{L S}^{n'}$ for all values of L and S .

The transformation matrix from the (J, M) system of representation to the (L, M_L, S, M_S) system is the same for both configurations. Hence the patterns of the two will be inverted with respect to one another.

It immediately follows that a configuration with half a closed shell of electrons is unsplit by any crystalline field in any of its states, excited or otherwise, provided the field satisfies Laplace's equation and that matrix elements of the crystalline field to other configurations are neglected.

If the n and n' systems add up to $\frac{1}{2}$ or $1\frac{1}{2}$ closed shells, only L values correspond. Hence the above theorem will only apply to the orbital pattern. Thus, for example,¹⁴ Ni^{++} and Co^{++} have patterns inverted with respect to one another provided the potential energy satisfies Laplace's equation. Van Vleck in this reference also gives other examples of the use of this theorem. Our proof is in fact an extension to the general case of the proof given by Van Vleck for these particular examples.

5. Matrix Elements of the Cubic Field.

The expression for the potential energy which we propose to use contains terms $c_{(4)}C_{(4)}$ and $c_{(6)}C_{(6)}$. The matrix elements of $c_{(4)}C_{(4)}$ have already been given by Penney and Schlapp⁵ for both the single-electron and many-electron problems. We need therefore only consider those of the other term.

Our calculations for a single electron were made using normalised hydrogen-like wave-functions $\frac{1}{\sqrt{2\pi}} f(r) e^{im\phi} P_{l, m}(\cos \theta)$. The matrix element divides into two parts, a radial integration involving c_6 which is diagonal in m , and an integration over θ and ϕ involving $C_{(6)}^i$.^{*} The final results, which required the expansion of $\cos^6 \theta P_{l, m}$, $\sin^4 \theta \cos^2 \theta P_{l, m}$ and similar expressions[†] in terms of associated Legendre functions, were as follows:

$$\overline{c_{(6)}} = c_{(6)} \langle l, m_l; l, m_l \rangle = \int c_{(6)} \{f(r)\}^2 r^2 dr \quad (13)$$

$$C_{(6)}^i(l_i, m_{l_i}; l_i, m_{l_i}) = 5 g(l_i, m_{l_i}) / 16(2l_i - 5)(2l_i - 3)(2l_i - 1)(2l_i + 3)(2l_i + 5)(2l_i + 7) \quad (14)$$

$$C_{(6)}^i(l_i, m_{l_i}; l_i, m_{l_i} - 4) = 15 h(l_i, m_{l_i}) / 16(2l_i - 5)(2l_i - 3)(2l_i - 1)(2l_i + 3)(2l_i + 5)(2l_i + 7) \quad (15)$$

where

$$g(l, m_l) = 66m_l^6 - m_l^4(90l^2 + 90l - 210) + m_l^2(30l^4 + 60l^3 - 120l^2 - 150l + 84) - \frac{10}{7}l(l-1)(l-2)(l+1)(l+2)(l+3) \quad (16)$$

$$h(l, m_l) = (-11m_l^2 + 44m_l + l^2 + l - 50) \sqrt{\frac{(l+m_l)! (l-m_l+4)!}{(l-m_l)! (l+m_l-4)!}} \quad (17)$$

¹⁴ Van Vleck, *Physic. Rev.*, 1932, 41, 210.

^{*} The suffix i denotes the i th electron and is not to be confused with the imaginary.

[†] Although these expansions are too long to print in full, the author will be pleased to send them to anyone requiring them. They are an extension of Devonshire's previously published expansions of $\cos^4 \theta P_{l, m}$, etc.¹⁵

¹⁵ Devonshire, *Proc. Roy. Soc. A.*, 1936, 153, 601.

The factor $\overline{c_6}$ is the same for all electrons in the same shell and is proportional to $\overline{r^6}$, the mean value of r^6 .

Similar formulæ hold for the many-electron systems for matrix elements diagonal in J in the (J, M) system of representation or for elements diagonal in L in the (L, M_L) system of representation, as we can again separate the radial part c_6 , e.g.,

$$\left. \begin{aligned} C_6(J, M : J, M) &= q_J g(J, M) \dots \\ C_{(6)}(J, M : J, M-4) &= 3q_J h(J, M) \dots \end{aligned} \right\} \text{where } C_{(6)} = \sum_i C_{(6)}^i \quad (18)$$

In the (L, M_L) system of representation, q_J is replaced by γ_L^n . For the fourth order field these constants are respectively p_J and β_L^n ,* and for $A_{(2)}$ they are σ_J and α_L^n .

The value of q_J in terms of γ_L^n is found by the spur method explained by Penney and Schlapp.⁵ The number γ_L^n which is the ratio of the matrix elements of the many-electron system to those of a single electron, is determined by another spur relation (eq. 11 of the previous section). In Table I. we have collected for the ground states of the configurations of f -electrons, values of the constants of the fields $A_{(2)}$, $C_{(4)}$ and $C_{(6)}$ and therefore of $A_{(4)}$ and $A_{(6)}$ which have the same diagonal elements as $C_{(4)}$ and $C_{(6)}$ respectively.

To determine $\overline{c_{(6)}}$ and $\overline{c_{(4)}}$ we require estimates of $\overline{r^6}$ and $\overline{r^4}$. Drs. Penney and Schlapp have kindly informed the writer that approximate values are $\overline{r^6} = 0.30 \times 10^{-48} \text{ cm.}^6$ and $\overline{r^4} = 0.32 \times 10^{-32} \text{ cm.}^4$. These they have obtained for a Ce^{+++} ion using the Fermi potential in conjunction with the W-K-B. method of approximating to a wave-function. To obtain values for the other rare-earth ions, we must apply corrections of rather unknown magnitude due to the changes in the structure of the ion. Spedding¹ suggests a factor of $(Z_{Ce}/Z_x)^4$ to allow for the contraction in $f(r)$ due to an increase in the effective nuclear charge Z_x , but this is certainly very approximate if only for the reason that Z is inaccurately known for f -electrons. We therefore prefer to assume that both $\overline{r^4}$ and $\overline{r^6}$ are constant for the whole series. This may in general require that the levels be multiplied by a simple factor to bring them in accordance with experiment, but this is of little importance for our present purpose.

The distance a depends upon the radii of the oxygen atom and of the rare earth ion. The former is 1.33 and the latter, which varies only slightly from one rare-earth to another, is, roughly, 1.15 Å. Hence an approximate value is $a = 2.50 \text{ Å}$. When this is substituted in the expressions (9) we obtain

$$\overline{C_4} = 3300 \text{ cm}^{-1}; \quad \overline{C_6} = -600 \text{ cm}^{-1}.$$

This value of a is probably an upper limit. Consequently, the ratio $\overline{C_6}/\overline{C_4} \propto \frac{1}{a^2}$ is unlikely to be less in magnitude than the value given by the above figures but may possibly be greater in the crystals we are considering.

* This is a slight change of the notation used by Penney and Schlapp, to facilitate extension to higher orders. They use q where we have β_L^n .

TABLE I.

Field.	L	5	6	3	L	3	6	5
	n_f	2	4	6	n	1	3	5
	γ_L^n	$-\frac{1}{3027024}$	$-\frac{5}{28540512}$	$-\frac{1}{61776}$	γ_L^n	$\frac{1}{61776}$	$\frac{5}{28540512}$	$\frac{1}{3027024}$
$C_{(6)}$	q_8	—	$\frac{3}{26}$	—	$q^{15/2}$	—	$\frac{12}{65}$	$\frac{6}{143}$
and	q_7	—	$\frac{1}{26}$	—	$q^{13/2}$	—	$\frac{21}{130}$	$-\frac{7}{143}$
$A_{(6)}$	q_6	$\frac{5}{22}$	$-\frac{3}{22}$	$\frac{7}{132}$	$q^{11/2}$	—	$\frac{38}{143}$	$-\frac{109}{143}$
(in	q_5	$\frac{3}{10}$	$-\frac{57}{130}$	$-\frac{7}{12}$	$q^{9/2}$	—	$\frac{969}{286}$	$-\frac{136}{143}$
terms	q_4	$\frac{136}{55}$	$\frac{3876}{715}$	$\frac{63}{22}$	$q^{7/2}$	$\frac{1}{7}$	—	$-\frac{68}{11}$
of γ_L^n)	q_3	—	—	$-\frac{49}{6}$	—	—	—	—
	β_L^n	$-\frac{1}{10395}$	$\frac{1}{32670}$	$-\frac{1}{990}$	β_L^n	$\frac{1}{990}$	$-\frac{1}{32670}$	$\frac{1}{10395}$
$C_{(4)}$	p_8	—	$\frac{99}{364}$	—	$p^{15/2}$	—	$\frac{33}{91}$	$\frac{2}{13}$
	p_7	—	$\frac{15}{52}$	—	$p^{13/2}$	—	$\frac{6}{13}$	$\frac{14}{143}$
and	p_6	$\frac{14}{33}$	$\frac{4}{11}$	$\frac{1}{33}$	$p^{11/2}$	—	$\frac{799}{1001}$	$-\frac{1}{143}$
$A_{(4)}$	p_5	$\frac{2}{3}$	$\frac{68}{91}$	$-\frac{1}{21}$	$p^{9/2}$	—	$\frac{340}{143}$	$-\frac{565}{2574}$
(β_L^n)	p_4	$\frac{21}{11}$	$\frac{476}{143}$	$-\frac{23}{154}$	$p^{7/2}$	$\frac{3}{7}$	—	$-\frac{52}{99}$
	p_3	—	—	$-\frac{1}{6}$	$p^{5/2}$	$\frac{11}{7}$	—	$\frac{13}{2}$
	p_2	—	—	$\frac{55}{21}$	—	—	—	—
	α_L^n	$\frac{2}{135}$	$-\frac{2}{495}$	$-\frac{2}{45}$	α_L^n	$\frac{2}{45}$	$\frac{2}{495}$	$-\frac{2}{135}$
$A_{(2)}$	σ_8	—	$\frac{11}{20}$	—	$\sigma^{15/2}$	—	$\frac{22}{35}$	$\frac{3}{7}$
	σ_7	—	$\frac{33}{52}$	—	$\sigma^{13/2}$	—	$\frac{99}{130}$	$\frac{6}{13}$
	σ_6	$\frac{15}{22}$	$\frac{87}{110}$	$\frac{5}{22}$	$\sigma^{11/2}$	—	$\frac{1020}{1001}$	$\frac{2643}{5005}$
	σ_5	$\frac{9}{10}$	$\frac{29}{26}$	$\frac{1}{6}$	$\sigma^{9/2}$	—	$\frac{35}{22}$	$\frac{15}{22}$
(α_L^n)	σ_4	$\frac{78}{55}$	$\frac{21}{11}$	$\frac{9}{154}$	$\sigma^{7/2}$	$\frac{5}{7}$	—	$\frac{39}{35}$
	σ_3	—	—	$-\frac{1}{6}$	$\sigma^{5/2}$	$\frac{9}{7}$	—	$\frac{39}{14}$
	σ_2	—	—	$-\frac{11}{4}$	—	—	—	—
	σ_1	—	—	$-\frac{9}{2}$	—	—	—	—

n_f = number of f -electrons.

$\gamma_L^n = -\gamma_L^{14-n} = +\gamma_L^{7+n} = -\gamma_L^{7-n}$, etc.

The α_L^n for $Ax^2 + By^2 - (A+B)x^2$ are obtained by replacing the factor 2 in the numerators of the α_L^n given above, by $(A+B)$.

6. The J-Multiplets for the Fields $C_{(4)}$ and $C_{(6)}$.

Using the matrix elements for $C_{(4)}$ and $C_{(6)}$ separately we have set up the secular determinants for all values of J up to $J = 8$ and we have obtained the levels into which each J -level is split by the two fields separately. The results for $J = 2, 3, \dots, 8$, are summarised in Table II.

TABLE II.

J.	Field.	Unit.	Irreducible Representations.				
			A_1 .	A_2 .	E .	T_1 .	T_2 .
2	$C_{(4)}$	p_2	—	—	14.4	—	—9.6
	$C_{(6)}$	—	—	—	—	—	—
3	$C_{(4)}$	$12p_3$	—	-12	—	6	-2
	$C_{(6)}$	$360q_3$	—	-4	—	0	8
4	$C_{(4)}$	$12p_4$	28	—	4	14	-26
	$C_{(6)}$	$360q_4$	-80	—	64	4	-20
5	$C_{(4)}$	$84p_5$	—	—	-6	7.856, -7.856	4
	$C_{(6)}$	$360q_5$	—	—	-96	52.22, -230.22	240
6	$C_{(4)}$	$12p_6$	66	-126	114	-96	102.074, -62.074
	$C_{(6)}$	$2160q_6$	176	16	-48	8	92, -132
7	$C_{(4)}$	$12p_7$	—	-20.8	-140.8	-205.95, 215.95	189.20, -98.80
	$C_{(6)}$	$1080q_7$	—	-832	176	185.584, -209.584	720.60, -536.60
8	$C_{(4)}$	$12p_8$	392	—	353, -297	-334.6, -29.37	367.40, -271.40
	$C_{(6)}$	$3960q_8$	-64	—	383, -208	95.73, -423.73	272.25, -140.25

and those for $J = \frac{5}{2}, \frac{7}{2}, \dots, \frac{15}{2}$ in Table III. States with J less than two are not affected by either of the two fields. The levels are placed in the tables under the irreducible representations of the octahedral group with which they are associated. These representations have been given by Bethe¹⁶ for various values of J , and in his notation are $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$ and Γ_5 for integral values of J and $\Gamma_6, \Gamma_7, \Gamma_8$ for half-integral values of J . For integral values, however, we prefer to use Mulliken's notation with molecular orbitals,¹⁷ i.e., A_1, A_2, E, T_1, T_2 , where $A_1 = \Gamma_1, A_2 = \Gamma_2$ are single levels, $E = \Gamma_3$ is doubly degenerate, $T_1 = \Gamma_4, T_2 = \Gamma_5$ are triply degenerate. If J is even we add a suffix g , and if J is odd a suffix u , e.g., A_{2u} or T_{1g} . There is no such notation for half-integral values as these do not occur in molecular orbitals.

It may be noted that, for a given value of J , a level associated with a representation which is *not* repeated is an "additive level" in the sense, that in the presence of a field $c_{(4)}C_{(4)} + c_{(6)}C_{(6)}$ the level can be merely obtained by adding the term values in the fields $c_{(4)}C_{(4)}$ and $c_{(6)}C_{(6)}$ separately. Thus, in the combined field one level of $J = 3$ is

$$-144p_3c_{(4)} - 1440q_3c_{(6)}.$$

¹⁶ Bethe, *Ann. Physik*, 1929, 3, 133.

¹⁷ Mullikan, *Physic. Rev.*, 1933, 43, 279.

TABLE III.

J .	Field.	Unit.	Irreducible Representations.		
			Γ_6 .	Γ_7 .	Γ_8 .
$\frac{5}{2}$	$C_{(4)}$	$12p_{5/2}$	—	—4	2
	$C_{(6)}$	—	—	—	—
$\frac{7}{2}$	$C_{(4)}$	$12p_{7/2}$	14	—18	2
	$C_{(6)}$	$360q_{7/2}$	—20	—12	16
$\frac{9}{2}$	$C_{(4)}$	$12p_{9/2}$	39.20	—	17.051, —36.561
	$C_{(6)}$	$720q_{9/2}$	—64	—	52.88, —20.88
$\frac{11}{2}$	$C_{(4)}$	$12p_{9/2}$	—84	44	77.20, —57.20
	$C_{(6)}$	$1080q_{11/2}$	16	176	40.54, —136.54
$\frac{13}{2}$	$C_{(4)}$	$12p_{13/2}$	—162	124.94, —54.94	155.005, —109.005
	$C_{(6)}$	$2160q_{13/2}$	$22\frac{6}{7}$	254.28, —240.56	89.65, —107.935
$\frac{15}{2}$	$C_{(4)}$	$12p_{15/2}$	294	—26	266.4, —141.5, —258.9
	$C_{(6)}$	$3960q_{15/2}$	—40	—312	274.2, 64.0, —162.2

This is more easily understood if we realise that the form of the wave-functions belonging to a non-repeated representation depends only on the symmetry and not on the order of the field. Levels associated with *repeated* representations are not additive in this sense even as an approximation. However, their determination is simplified by a knowledge of the additive levels, because both types usually occur together as roots of the small determinants of the fourth or fifth order into which the secular determinant factorises.

Although the number of levels and the degeneracy of each is, of course, the same for $C_{(4)}$ and $C_{(6)}$ the relative positions of corresponding levels may differ considerably. For this reason it may sometimes be important to include $c_{(6)}C_{(6)}$ even though the overall splitting which it produces is much smaller than that caused by $c_{(4)}C_{(4)}$. Thus the curve giving the variation of the paramagnetic susceptibility of a salt with the temperature depends at low temperatures mainly on the lowest level and those next above it. If the inclusion of sixth order terms brings the lowest levels much closer together the whole appearance of the theoretical curve may be changed. We shall see later in the case of Ho^{+++} that a single, a doubly degenerate and a triply degenerate level are brought within 2 cm.^{-1} of one another by the particular combination of $C_{(4)}$ and $C_{(6)}$ which we are using.

7: The J-Multiplets in the Combined Field:

To obtain levels in a combined field $c_{(4)}C_{(4)} + c_{(6)}C_{(6)}$ we must add the corresponding matrix elements of the fourth and sixth order fields and expand the secular determinant so obtained. Some of the roots of the determinant will be "additive" and are therefore known immediately but, if J is greater than 4, the existence of other roots means that in general the complete determinant must be set up and expanded for the particular field under consideration.

We have assumed a field such that $\bar{c}_4 = 3300 \text{ cm.}^{-1}$ and $\bar{c}_6 = -600 \text{ cm.}^{-1}$ for all the triply-ionised rare-earth ions. The results for all the ions in their ground state and in one case in an excited state are given in Tables IV. and V., together with those for a field such that $c_4 = 3300 \text{ cm.}^{-1}$ and $\bar{c}_6 = 0$. We cannot compare our results with experimental

TABLE IV.*

Rare-earth Ion.	n.	Ground State.	Field.	Irreducible Representations.				
				A_1 .	A_2 .	E .	T_1 .	T_2 .
La	0	1S_0	V_1 V_2	—	—	—	—	—
Pr	2	3H_4	V_1 V_2	-217.76 -203.6	—	-17.80 -29.1	-101.11 -101.32	185.57 189.1
Il	4	5I_4	V_1 V_2	96.562 112.97	—	29.268 16.14	57.308 56.49	-109.007 -104.9
Eu	6	$^7F_{0,1}$	—	—	—	—	—	—
Tb	8	7F_6	V_1 V_2	76.004 80	-153.090 -152.73	139.272 138.18	-116.55 -116.36	123.94, -75.54 123.726, -75.241
Ho	10	5I_8	V_1 V_2	-126.146 -129.266	—	-124.45, 97.50 -116.405, 97.939	126.45, 29.364 110.337, 9.685	-125.031, 97.50 -121.154, 89.497
Ta	12	3H_6	V_1 V_2	89.54 106.67	-205.19 -203.63	188.91 184.24	-155.93 -155.15	166.17, -97.63 164.97, -100.322
Cp	14	1S_0	—	—	—	—	—	—

* Fields : V_1 is such that $\bar{C}_{(4)} = 3300 \text{ cm.}^{-1}$; $\bar{C}_{(6)} = -600 \text{ cm.}^{-1}$. V_2 is such that $\bar{C}_{(4)} = 3300 \text{ cm.}^{-1}$; $\bar{C}_{(6)} = 0$. Values are in cm.^{-1} .

results as few, if any, experiments have been made on crystals with internal fields of cubic symmetry and therefore magnetically isotropic. Those used by Spedding and his collaborators, for example and other salts, are magnetically anisotropic to a considerable degree. As pointed out by Dr. Penney and the writer elsewhere,¹⁸ this fact alone indicates that the agreement between the theoretical results for a field $C_{(4)}$ and the experimental results is partly fortuitous. We shall, however, illustrate the main features of our results and the complications likely to occur by referring to these experiments.

On account of its origin an internal cubic electric field of the fourth order, where $c_{(4)}$ is positive, is almost certainly accompanied by a field $c_{(6)}C_{(6)}$ in a ratio $c_{(6)}/c_{(4)}$ similar to that given by the six-atom model. For a cubic field arising from eight atoms at the corners of a cube $c_{(4)}$ is negative, but the ratio $c_{(6)}/c_{(4)}$ still has the same sign as before and a slightly smaller magnitude. Consequently, if a small field of the latter type is superposed on the six-atom field, so that the resulting value of $c_{(4)}$ is still positive, the ratio of $c_{(6)}/c_{(4)}$ will certainly not be decreased. Now Spedding, Hamlin and Nutting⁴ have found levels 0, 77, 260 cm.^{-1}

¹⁸ Penney and Kynch, *Nature*, 1937, 140, 109.

TABLE V.*

Rare-earth Ion.	<i>n</i> .	Ground State.	Field.	Irreducible Representations.		
				Γ_6 .	Γ_7 .	Γ_8 .
Ce	1	$2F_{5/2}$	V_1 V_2	—	—251·4 —251·4	125·7 125·7
Nd	3	$4I_{9/2}$	V_1 V_2	—95·46 —112·975	—	—61·73, 109·46 —49·14, 105·625
Sm	5	$6H_{5/2}$	V_1 V_2	—	—99·05 —99·05	49·52 49·52
	5	$6H_{7/2}$	V_1 V_2	—36·836 —28·013	30·724 36·017	3·056 —4·002
Gd	7	$8S_{7/2}$	V_1 V_2	—	—	—
Dy	9	$6H_{15/2}$	V_1 V_2	—173·627 —172·310	4·963 15·238	—153·79, 85·06, 154·06 —156·13, 82·93, 151·74
Er	11	$4I_{15/2}$	V_1 V_2	126·157 129·231	—35·405 —11·429	124·43, —58·67, —111·13 117·10, —62·20, —113·80
Yb	13	$2F_{7/2}$	V_1 V_2	—250·02 —240	302·57 308·57	—26·29 —34·29

* Fields as in Table IV. Values are in cm^{-1} . All levels in this table are doubled by the Kramer's degeneracy.

for $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ comparing well with relative values of 0, 76, 260 cm^{-1} for a field $C_{(4)}$. With the combined field, on adjusting to 260 cm^{-1} the overall splitting of this state of Nd^{+++} , we find that the middle level is at 45 cm^{-1} . If we assume that a cubic field will explain the observations, in order that the level should come within the experimental error (about 5 cm^{-1}) of 77 cm^{-1} the amount of the sixth order field must be reduced to $1/5$ or less, and this seems unlikely. In the case of erbium the levels are (0, 19, 41, 85) experimentally¹; (0, 19, 38, 85, 89) with $c_{(4)}$, and (0, 19, 27, 85, 85·6) with the combined field. One level has again shifted considerably, and the two highest levels are very close. Both these provide examples of the chief effect of the extra field term $C_{(6)}$.

The absorption spectra of gadolinium sulphate shows peculiarities which cannot easily be explained. The configuration of the Gd^{+++} ion, $4f^7$, is not split in any of its many states, whether excited or otherwise, by a field satisfying Laplace's equation. Experiment has shown that the spectrum of gadolinium sulphate¹ is no simpler, and that in some of the multiplets the number of lines is even greater, than in the case of other rare-earth salts. The number of lines in the multiplets is certainly greater and the intervals between the lines smaller than would be expected from the degenerate J -levels alone.

Unless the spectrum arises by transitions from a configuration $4f^7$ to a configuration $4f^65d$ or $4f^66p$ we must suppose that the number of levels between which transitions can take place has been increased in some way. For this to occur the degeneracy of the J -levels must have been removed

or the levels doubled. The degeneracy could be removed if the field did not satisfy Laplace's equation. In this case, however, as we showed in §2, the terms of lowest order and of most importance, the cubic fourth order term and probably the second order term, produce the same effect as $C_{(4)}$ and $A_{(2)}$ respectively except for a bodily displacement. Consequently they only displace the levels and do not split them. The effect of the remaining terms is difficult to estimate but we should remember that the deviations from Laplace's equation are probably in any case small. The degeneracy can also be removed by interactions between the different types of coupling of the $4f^7$ group of electrons, although these too are small. Finally, there are the possibilities that the number of levels is increased by interaction with the vibrations of the ion in the crystal, or because there is more than one gadolinium ion per unit cell of the crystal, the atoms not being all equivalent. This last cause, may increase the number of levels considerably and should be easily detectable.

These suggestions are all invoked to support an interpretation of the spectrum by the improbable transitions between different $4f^7$ configurations. If the character of the spectrum were suitable it would be simpler to assume transitions to a configuration involving $4f^6$. Recently, however, Freed and Mesirov¹⁹ have found that the lines are diffuse in experiments with Ce^{+++} and Yb^{+++} where transitions must be to a $5d$ or higher state since there can be no change of coupling between the electrons. Their result seems to show that the sharp line absorption spectrum of gadolinium sulphate is due only to transitions between configurations $4f^7$, whose levels must be split and multiplied by the causes outlined above. This question has been treated at length by Van Vleck,¹² who also comes to this conclusion.

The hypothesis of two ions per unit cell of the crystal may possibly explain why five low-lying levels are found in $Sm_2Cl_3 \cdot 6H_2O$.²⁰ If the two ions were not equivalent and were subject to a rhombic field we should obtain precisely this number of levels. In the case of Sm^{+++} , the level $J = 7/2$ is only about 300 cm^{-1} above the ground state. As, however, the splitting of the higher level is smaller than that of the lower in either fields of the second or fourth orders, the lowest level of the pattern for $J = 7/2$ is probably not sufficiently low to explain any of the experimental levels except the level at 315 cm^{-1} .

8. Conclusion.

We have now obtained the structure of the various J -levels of the metallic ions of rare-earth crystals with cubic internal electric fields of the fourth order or of the sixth order and also when the field is a simple combination of these two orders which is likely to occur in certain cases. A comparison of this structure with that obtained experimentally for some rare-earth crystals, especially sulphates, has shown the many complications which may arise. These are due to the superposition on the pattern for a crystalline field of several other effects among which we have mentioned the coupling to the electronic states of the vibration frequencies of the ion in the crystal and the possibility of several non-equivalent ions in a unit cell of the crystal, as in the case of copper sulphate. Although at present the quantitative effects of these causes

¹⁹ Freed and Mesirov, *J. chem. Physics*, 1937, **5**, 26.

²⁰ Spedding and Bear, *Physic. Rev.*, 1932, **42**, 76.

is uncertain, the qualitative effect is known. Hence our patterns should form a basis from which to start to disentangle the effects one from another. We mention also that some anomalies will arise in a comparison with our basic patterns owing to the insensitivity of present experimental methods. If two levels are within 2 or 3 cm^{-1} of each other, as often occurs, it is difficult to separate them experimentally, unless the number of lines arising from them in the spectrum is very large. This apparent degeneracy, however, may be removed by the other superimposed effects stated above.

We have also assumed that the non-cubic terms in the crystalline potential are small. This definitely means that our analysis is only valid for crystals in which the ion is surrounded by six similar atoms, probably, oxygen atoms, on precisely the same footing. In many crystals, for example the sulphates, this is not true and these cases the model should not be applied even as an approximation to a more detailed calculation. A good test of the size of the non-cubic terms is the degree of the magnetic anisotropy, and if this is small in general we are justified in assuming that the non-cubic terms are also small. A large number of crystals of the rare-earth salts are monoclinic. These will contain at least two ions per unit cell of the crystal and, in consequence, we may expect slight deviations from perfect equality of the atoms surrounding the ion even if the crystal satisfies all our requirements. Such deviations, however, will not be great if the atoms are from the same source. This is irrespective of the doubling and the removal of the degeneracy which may occur with two or more non-equivalent ions.

The absolute magnitude of the most important term in the field is proportional to $1/a^5$ where a is the distance between the ion and any of its six neighbours. We have assumed $a = 2.5$ A.U. but, although approximately the same for all the rare-earths in the same salt, it is probably less than this. Thus the absolute magnitude of the field should, if anything, be greater than that we have used in our calculations. The ratio $c_{(6)}/c_{(4)}$ should also be slightly increased.

In conclusion, the author wishes to express his gratitude to Dr. W. G. Penney for suggesting this problem and for his discussion of various parts of the paper.

Summary.

The patterns of all J -levels are given for the rare-earth ions in crystalline electric fields of cubic symmetry, either of the sixth order or of the fourth order, together with the constants necessary to evaluate the levels in particular cases. The combination of the two fields appropriate to an octahedral field due to six point charges is then obtained and applied to the ground levels of these ions. In the subsequent discussion it is shown that the experimental results for the hydrated sulphates of the rare-earths cannot be satisfactorily explained on the assumption of a cubic field although this assumption may be satisfactory for other crystals.

In addition some general theorems on the matrix elements of crystalline potential energies and on the inversion of the patterns of complementary configurations are proved.

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THE REDUCTION OF CHROMIUM OXIDE.

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As evidence accumulates concerning the adsorption of reactants on the surface of solid catalysts, it becomes increasingly clear that there is a very close similarity between reactions which are examples of true contact catalysis and those in which a gas is reacting with a solid. Attention was drawn to the significance of such a comparison by the experiments of Rhead and Wheeler¹ and of Shah² on the combustion of carbon, while more recent experiments by Barrer³ have dealt with the behaviour of hydrogen and oxygen on surfaces of diamond and graphite.

The significance of reaction between a catalyst and one or more reactants undergoing changes on it was also pointed out by Kingman,⁴ who showed that the adsorptive capacity for hydrogen of catalysts prepared from mixtures of zinc oxide and chromium oxide depended greatly on the degree of reduction which the solid had undergone. These results indicated that adsorption of hydrogen played an important part in the reduction of the mixed oxides. McKinney⁵ found that adsorption of carbon monoxide on Pd oxide was necessary before any reduction took place. When hydrocarbon vapours come into contact with chromium oxide it has been found⁶ that the extent of reduction depends on the particular hydrocarbon used and has a still more important influence on the catalytic activity of the solid; the present investigation was undertaken in order to determine the mechanism of the reactions involved, and to compare the behaviour of different hydrocarbons with that of hydrogen.

Experimental Methods.

Chromium hydroxide was prepared by adding a slight excess of aqueous ammonia to a solution of chrome-alum of analytical reagent quality; the precipitate was washed free from sulphate, dried in a steam oven and ground to a fine powder in a paint mill. It was then made into small pellets $\frac{1}{8}$ in. diam. by extruding it, in a paste with distilled water, drying and breaking up the threads produced. A single batch of hydroxide containing 33.6 per cent. Cr was used throughout the series of experiments. The properties of chromium hydroxide are known to depend largely on its method of preparation,⁷ so that the use of a standard product is important.

The chromium hydroxide pellets (about 1 g. weight) were heated in a hard glass tube placed in an electric furnace, and the gas or vapour under investigation was passed over them at a steady rate while the temperature was raised to 450°. The rate of dehydration was first determined by heating in pure nitrogen; separate specimens of the hydrated oxide were then heated in turn in a stream of nitrogen containing hydrogen, hexane, benzene, cyclohexane and dekaline. This procedure was found to be

¹ *J. Chem. Soc.*, 1913, 103, 461.

² *Ibid.*, 1929, 2663, 2676.

³ *Proc. Roy. Soc., A*, 1935, 149, 253; *J. Chem. Soc.*, 1936, 1256, 1261.

⁴ *Trans. Faraday Soc.*, 1931, 27, 654.

⁵ *J.A.C.S.*, 1933, 55, 3626.

⁶ Griffith, *Trans. Faraday Soc.*, 1937, 33, 412.

⁷ Kohlschütter, *Z. angew. Chem.*, 1936, 49, 865.

preferable to studying the reduction of dehydrated material on account of the economy of time, and of possible changes in the character of the solid during dehydration.

The rate of passage of gas over the solid was 3600 c.c./hour at N.T.P. in every case, the partial pressure of hydrogen or hydrocarbon being kept at 100 mm. The necessary concentration of hydrocarbon was attained by use of a saturator kept at a suitable temperature in a thermostat, with the usual precautions to prevent condensation of any liquid. For tests with hydrogen a mixture of hydrogen and nitrogen was compressed into a storage cylinder at about 100 atms. from which it was drawn as required.

Purification of Reagents.

Nitrogen was stored under pressure over hydroquinone solution and was found by analysis to contain no oxygen. It was passed through softolite and calcium chloride tubes before reaching the reduction furnace.

Hydrogen was passed through alkaline sodium hydro-sulphite solution and strong calcium chloride solution before being dried in a calcium chloride tower; it was then passed over a copper catalyst at 800° and finally dried as in the case of nitrogen. Oxygen was found to be absent on analysis.

Benzene was of analytical reagent quality, dried by long storage over calcium chloride; cyclohexane was fractionated by means of a Dufton column, the portion boiling from 81° to 82° being used after drying. Hexane was also redistilled and dried. Dekalin was fractionated to give the *cis*-isomer b.pt. 190°-192°.

Measurement of Oxygen Removal.

On heating the oxide in nitrogen or hydrogen, determinations were

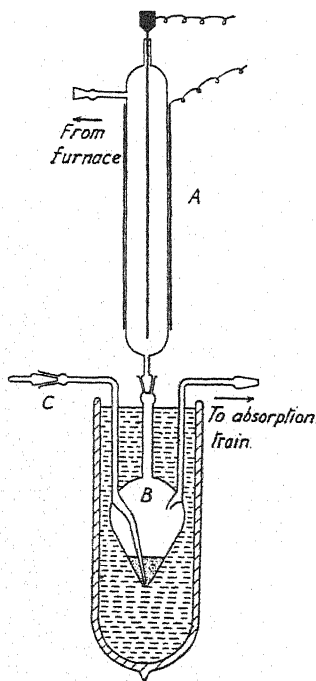


FIG. 1.

made simply of the water evolved by means of CaCl_2 tubes, but with the hydrocarbons, carbon dioxide was also formed and had to be measured with soda lime. Care was taken that the absorption tubes were always higher in temperature than the saturator in which hydrocarbon vapour was picked up by nitrogen. No traces of organic decomposition products, such as oxygen-containing intermediate derivatives from the hydrocarbons, could be detected in the absorption tubes. In the experiments with dekaline, difficulties were experienced owing to the condensation of excess hydrocarbon at the outlet of the reduction tube. The system eventually adopted for runs with dekaline is shown in outline in Fig. 1, and consisted of a small electrostatic precipitator A connected to the trap B which was immersed in a Dewar flask containing acetone-solid CO_2 mixture, and followed by CaCl_2 and softolite tubes. A series of these traps was used during an experiment, each one being removed when it was nearly full of condensed dekaline and water. The water content was subsequently determined by passing a stream of dry air through the trap (warmed to room temperature) via tube C into a CaCl_2 tube; under these conditions no condensation of dekaline took place in the absorption tube, but every tube had to be conditioned, before

it was weighed in the first place, by being treated with dekaline vapour.

As the absorbent material had a small retentive capacity for hydrocarbons this technique was applied with other hydrocarbons also. Direct comparison of the rates of reduction with dekaline and with the other hydrocarbons is not possible owing to the different technique adopted in determination of water.

Results Obtained.

In Fig. 2 the experimental results are summarised, the total oxygen removed being plotted against time. In every case the oxide was raised from room temperature in the appropriate atmosphere, to 450° at a steady rate; this took approximately 60 minutes.

The curve for nitrogen, 5, was used as the dehydration curve, the true values for the rates of reduction being obtained by subtracting the figures of curve 5. It is evident that the reduction of chromium oxide is more extensive with any hydrocarbon than it is with hydrogen, but that cyclohexane and benzene are the least effective of the organic reducing agents.

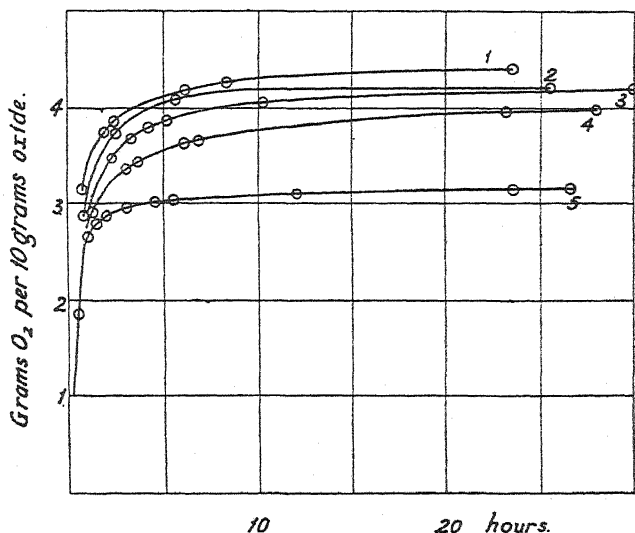


FIG. 2.—1. Hexane. 3. Benzene.
2. Cyclohexane. 4. Hydrogen.
5. Nitrogen.

This observation agrees with the differences in colour of the reduced oxide; after treatment with hydrogen the residue is green-yellow, after cyclohexane or benzene it is brown and after the other hydrocarbons it is black.

A closer study of the reduction reactions can be made from the figures given in Table I, where the total weight of oxygen removed at different time intervals is shown in its distribution as water or carbon dioxide. The most interesting feature of this table is that with cyclohexane, benzene and hexane the extent of reduction due to water formation is much less than with hydrogen alone, and that practically no water formation occurs after 2 hours' treatment; the apparent slight decrease in the amount of water in some cases is due to small differences in the rate of heating to 450° . Owing to experimental difficulties with dekaline the figures cannot be regarded as so accurate as with the lower boiling hydrocarbons, but it can be seen that reduction with hydrogen continues much longer.

TABLE I.—TOTAL GRAMS OF OXYGEN REMOVED FROM 10 GRAMS OF CHROMIUM OXIDE: DISTRIBUTION AS CARBON DIOXIDE OR AS WATER.

Time Hours.	Reducing Atmosphere.								
	Hydrogen As H ₂ O.	Cyclohexane As H ₂ O. As CO ₂ .		Hexane As H ₂ O. As CO ₂ .		Benzene As H ₂ O. As CO ₂ .		Dekalin As H ₂ O. As CO ₂ .	
2	0.15	0.5	0.25	0.53	0.32	0.21	0.31	—	—
3	0.41	0.55	0.33	0.61	0.35	0.21	0.48	0.52	0.07
4	0.57	0.54	0.42	0.65	0.37	0.23	0.54	0.74	0.11
5	0.67	0.54	0.49	0.68	0.39	0.26	0.58	0.85	0.15
10	0.72	0.49	0.52	0.69	0.46	—	—	0.98	0.31
15	0.76	0.45	0.52	0.67	0.53	—	—	0.98	0.38
20	0.79	0.45	0.52	0.66	0.58	—	—	—	—
25	0.82	—	—	0.63	0.62	0.30	0.65	—	—

Adsorption on Reduced Oxides.

As a means of further inspection of the solid product after the reductions, the adsorption of benzene on the oxide obtained after treatment with hydrogen, and after hexane, was determined. The general form of apparatus was that used in previous experiments,⁸ but a special gauge was developed in order to make velocity measurements possible. This is of the McLeod type and is shown in Fig. 3. The mercury is raised to the level X in B, and the level reached in the tube C is read by means of a milk-glass scale behind it. The whole gauge is heated in a steam jacket E, having a reflux condenser at G. Mercury vapour is prevented from entering the rest of the system by a small condenser H.

The pressure, in cm., is given by the relation

$$p = \frac{0.9865 AL^2}{V - \frac{v_2}{v_1} AL} + 0.028$$

where A is the volume in c.c. per cm. length of the tube C, L the difference in length, in cm., of mercury in C and the point X (level with top of C), V the volume cut off in bulb A and tube C, v_1 the volume of whole adsorption apparatus to point X, and v_2 the volume of whole adsorption apparatus to cut off, excluding bulb A and tube C, with temperature correction of the hot part to room temperature.

The factor 0.9865 is the ratio of the density of mercury at 100° to that at 20°. The additional 0.028 cm. is the vapour pressure of mercury at 100°.

For use with benzene, convenient dimensions were found to be $A = 0.1770$ c.c. per cm., $V = 10.82$ c.c., tube C 20 cm. long. In an example, with $L = 17.00$, $v_2 = 50.2$ c.c., $v_1 = 46.56$, then $p = 6.684$ cm. The compression in the

gauge must not lead to condensation of vapour, and although the gauge was not above the critical temperature of benzene, calibrations showed that

⁸ Griffith and Hill, *Proc. Roy. Soc., A*, 1935, 148, 194.

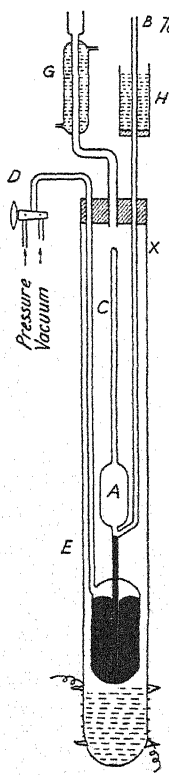


FIG. 3.

the instrument was satisfactory if benzene vapour was drawn from liquid at 3° below room temperature.

About 0.25 g. of chromium oxide was evacuated at 450° for 2 days at pressures below 0.001 cm. Benzene was admitted to the adsorption bulb, and the evacuation was repeated before any measurements were made.

Results Obtained.

In Fig. 4 are given the isobars for the adsorption, corrected to 45 mm. from the appropriate isotherm, of benzene on two samples of chromium oxides: 1. and 2. after reduction with hydrogen, and 3. after reduction with hexane. Fig. 5 shows specimen velocity curves, from which the isobars were derived. The hydrogen-reduced oxide shows van der Waals adsorption as the main feature up to 300° , but activated adsorption can be detected at 350° upwards. At 375° however decomposition sets in, as shown in the ultimate downward slope of the velocity curve, corresponding with further reduction of the oxide by the benzene. Although saturation on the oxide after reduction with hexane is rapid, adsorption velocities are also measurable, but a real separation of the two types of adsorption is not possible. There is no evidence of any further reduction and the extent of activated adsorption is probably small at temperatures up to 400° . The importance of the state of reduction of an oxide in determining its properties is emphasised by these results, and it is also clear that activated adsorption of benzene precedes its reducing action; this agrees with Kingman's observations for reduction by hydrogen.⁴

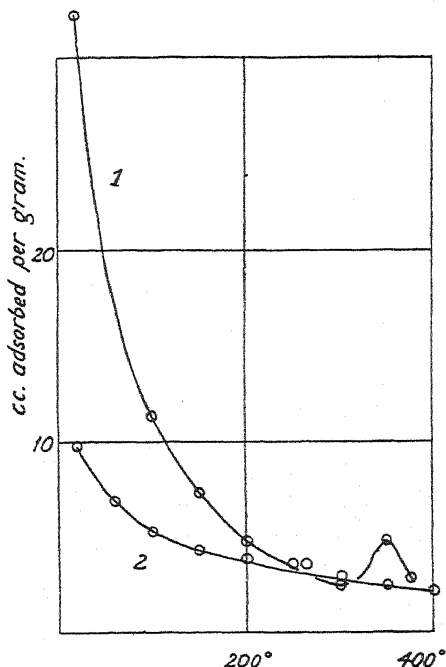


FIG. 4.—Adsorption Isobars for Benzene on Chromium Oxide.

1. After reduction in Hydrogen.
2. After reduction in Hexane.

The 375° point on curve 1 is the maximum value obtained before decomposition set in.

Discussion of Results.

The facts arrived at by these two methods of investigation may be summarised as follows:—

(1) When chromium oxide is reduced, activated adsorption of the reducing agent takes place before any reaction occurs. The occurrence of this type of adsorption with a large hydrocarbon molecule is established.

(2) The extent of reduction depends on the particular reducing agent employed, hydrocarbons being more effective than hydrogen. No evidence was found for the production of oxygen-containing organic compounds.

The possibility that the differences were due to changes in the diffusivity of water vapour or carbon dioxide in the various reducing atmospheres can be discounted, as the diffusivity would be much greater in hydrogen than in any hydrocarbon, and the reduction should therefore proceed more rapidly in hydrogen if this were the controlling factor. Also the rate at which oxygen is removed is not under discussion, and the diffusion velocity does not affect the final value reached after 20 hours or more. The use of gas mixtures containing 87 per cent. of nitrogen, and of hydrocarbons with very similar molecular weights further reduces the effect of the diffusivity factor even as far as reduction rates are concerned.

In order to avoid possible complications due to thermal effects of the reduction leading to overheating of the solid, the procedure of warming

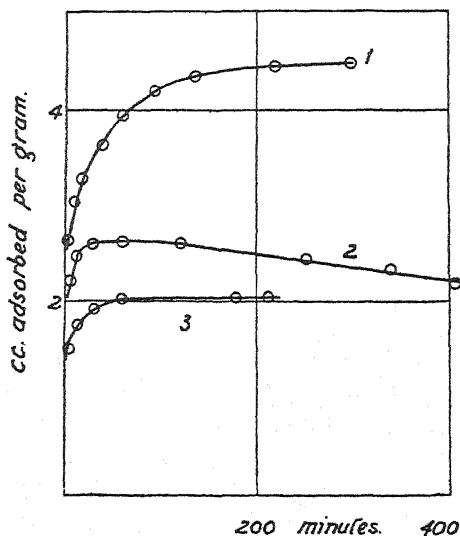


FIG. 5.—Rate of adsorption of Benzene.

1. Oxide reduced in Hydrogen. Adsorption at 350°.
2. Oxide reduced in Hydrogen. Adsorption at 375°.
3. Oxide reduced in Hexane. Adsorption at 400°.

and benzene is as effective as cyclohexane. When the reaction products are desorbed the carbon-carbon links are completely broken.

(4) No indication of an autocatalytic effect of a second solid phase can be found.

These conclusions may be compared with those of other investigators; Morikawa, Benedict and H. S. Taylor⁹ studied the behaviour of hydrocarbons on nickel catalysts and deduced that activated adsorption involved dissociation into hydrocarbon fragments, fracture of the carbon-carbon link involving a higher activation energy than of the carbon-hydrogen link. Balandin and Brussov¹⁰ investigated the dehydrogenation of cyclohexane and suggested that two types of catalyst were

slowly to 450° from room temperature was followed; this temperature was chosen as one at which the rate of reduction was always slow; in the stages of the reaction taking place after this heating up period, the extent of change with the diluted reaction gases was always very small in comparison with the thermal capacity of the system. It was also found that the green oxide fully reduced in hydrogen underwent further change in contact with hydrocarbons.

(3) The reducing action of hydrocarbons is largely due to the formation of carbon dioxide from them, and this indicates the existence of a carbon-oxygen link between the solid and the adsorbed hydrocarbon. The hydrogen produced in the decomposition of cyclohexane does not take part in the reduction,

⁹ *J.A.C.S.*, 1936, **58**, 1445, 1795.

¹⁰ *Z. physik. Chem.*, B, 1936, **34**, 96.

effective. One type must be a crystalline substance with a particular lattice on which the hydrocarbon molecule can be adsorbed in a flat position; the other type, which functions at a higher temperature, need not be crystalline but must hold the molecule simultaneously at two points. The dehydrogenation of cyclohexane on chromium oxide is attributed to decomposition in the second way.

It appears from the present investigation, however, that more specific properties are required in the chromium oxide catalysts. A previous publication⁶ has shown that cyclo-hexane is vigorously decomposed by chromium hydroxide at 500°, but that when the catalyst has previously been in contact with hexane, so that it is more fully reduced, the activity is practically negligible. The fact that the hydrocarbons behave as reducing agents chiefly by formation of carbon dioxide must be remembered when discussing the catalytic activity of the oxide, as this suggests that the surface is completely covered with hydrocarbon to the exclusion of hydrogen.

The distinction between activated adsorption and compound formation becomes increasingly difficult to make in view of these results.

Summary.

The rate of reduction of hydrated chromium oxide with hydrogen, hexane, cyclohexane, benzene and dekaline has been measured. The extent and velocity of reduction are greater with hydrocarbons than with hydrogen. Complete breakdown of the hydrocarbon molecule takes place, carbon dioxide being formed.

The adsorption of benzene on the oxide which has been reduced with hydrogen is compared with that on a specimen reduced by hexane, and it is found that adsorption of the hydrocarbon precedes the reducing action.

A modified McLeod gauge is described which can be used for accurate pressure determinations with a condensable vapour.

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THE FLUORESCENCE EFFICIENCIES OF SOLUTIONS OF HYDROCARBONS.

By E. J. BOWEN AND J. W. SAWTELL.

Received 29th July, 1937.

It has been shown by Bowen¹ that a screen of a suitable fluorescent material placed before a photo-cell removes the variation of sensitivity to wave-length of the cell over a particular region, and that the arrangement may be used as a relative quantum counter for the comparison of beams of ultraviolet light. Further measurements in this laboratory have shown that a screen composed of a layer of large crystals of uranyl potassium sulphate, $K_2SO_4 \cdot UO_2SO_4 \cdot 2H_2O$, about 1 mm. thick, enclosed between a quartz plate and an 'Ilford' "Delta" filter, placed in front of a modern potassium photo-cell, provides uniformity to wave-length to within a few per cent. over the range 4400 to 2450 Å. From a saturated solution of

¹ *Proc. Roy. Soc., A*, 1936, **154**, 349.

the substance strongly acidified with sulphuric acid non-regular hexagons about 1 mm. thick and 3-4 mm. across may be grown at the ordinary temperature, and the crystals built up into a rough mosaic to form the screen. Any light which passes between the crystals is removed by the "Delta" filter, which freely transmits the green fluorescent light.

Fig. 1 illustrates the apparatus for measuring the absolute efficiency of fluorescence of a solution of a hydrocarbon such as anthracene. Light from a mercury lamp was filtered and condensed at an angle of 45° on to the surface of a quartz cell containing the solution. The fluorescent light emitted normally to the surface was measured by a photo-cell and screen. The light filters used have already been described,¹ except that somewhat stronger nickel-cobalt solutions were found preferable, and for the 2650 Å. line the mercuric chloride solution was replaced by one of potassium iodide, 1.7 gm. per litre. A G.E.C. photometer unit consisting of a K.M.G. 7 (gas-filled potassium) photo-cell, high resistance (100 megohms) and an electrometer triode sealed in an evacuated bulb, was found very suitable for the work. Some measurements were made with other potassium and caesium photo-cells connected to an electrometer triode or to a Mullard P.M. 1 H.F. valve in the ordinary way, but the steadiness of the galvanometer zero was never good at the sensitivities used. To measure the

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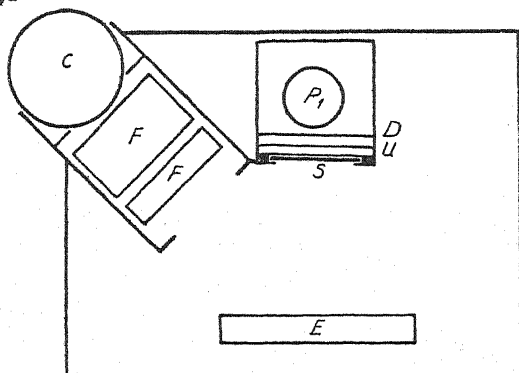


FIG. 1. — L. Mercury lamp. C. Quartz flask light condenser. F. Light filters. E. Cell containing fluorescent solution. S. Shutter. P_1 . Photo-cell for measuring fluorescence. U. Fluorescent screen of potassium uranyl sulphate. D. Ilford Delta filter.

absolute efficiency of a solution (concentrated enough to ensure that all the light was absorbed in a thin layer) the fluorescent light was first measured and then compared with the light scattered from a plate smoked with magnesium oxide, placed in the position occupied by the solution. Comparisons of the fluorescence of solutions of aesculin and of uranin and of the scattering from the magnesium oxide at different wave-lengths showed that the latter scattered ultraviolet light in the range used with the same efficiency as the visible. If a perfectly efficient scatterer is compared with a perfectly efficient fluorescent solution in this way the ratio of the measurements can be shown² to be ideally 4:1. The ratio is reduced to about 3.5:1 when allowance is made for the efficiency of scattering of magnesium oxide at 45° illumination (0.90) and for the fact that the emitting and collecting surfaces were of diameters not small compared with their distance apart.

In Fig. 2 is shown an apparatus in which relative measurements of fluorescence efficiency can be made at very small concentrations. A solution absorbing between 30 and 70 per cent. of the (normally) incident monochromatic light was placed in the cell E (2 cm. thick) and the amount of absorption measured by the integrating screen A and photo-cell P_2 . For this screen a solution of aesculin in water (1 gm./litre) in a cell 1 cm.

² Cf. Wawilow, *Z. Physik*, 1927, 42, 311; 1924, 22, 266.

thick, followed by a piece of didymium glass, was found most suitable to minimise the correction necessary for the yellow light unavoidably transmitted by the ultraviolet filters F. The fluorescence of the solution was measured at right-angles to the incident light by means of a screen and photo-cell. The disadvantage of this method is the limited range of concentrations which can be used with it, as with strong solutions the fluorescence is confined to the front face of the cell E, and with very dilute solutions the measurement of the amount of light absorbed cannot be made accurately.

The materials used were as follows: Benzene, "B.D.H. Extra pure." Naphthalene, a "pure" commercial specimen was recrystallised twice from alcohol, converted into the picrate, recrystallised from alcohol, the naphthalene liberated with sodium hydroxide solution, and again recrystallised from alcohol. Anthracene was freed from chrysogen by boiling with animal charcoal in benzene several times and recrystallising twice from benzene. Phenanthrene, commercially "pure", was recrystallised from alcohol, converted into the picrate, recrystallised from alcohol, the phenanthrene liberated and again recrystallised from alcohol. Fluorene, commercially "pure," was recrystallised three times from glacial acetic acid. Triphenylmethane was recrystallised twice from benzene and twice from alcohol. Hexane was prepared from "B.D.H.

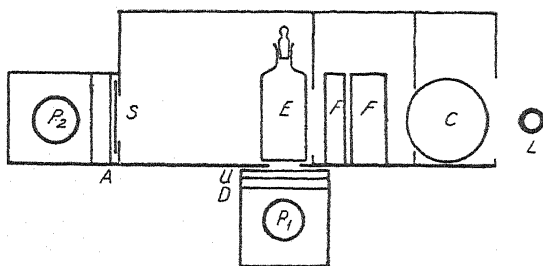


FIG. 2.— P_2 . Photo-cell for measuring light absorption. A. Fluorescent screen of æsculin solution. S. Shutter. E. Cell containing fluorescent solution. F. Light filters. C. Quartz flask light condenser. L. Mercury lamp. U. Fluorescent

screen of potassium uranyl sulphate. D. Ilford Delta filter. P_1 . Photo-cell for measuring fluorescence.

Hexane, free from aromatic hydrocarbons" by shaking for 24 hours with 10 per cent. potassium permanganate solution, then shaken with oleum for 24 hours, the hexane being separated, washed, dried with phosphorus pentoxide, and fractionally distilled. The ethyl alcohol was prepared by the method of Leighton, Crary, and Schliff.³

In Table I are given the results of measurements of the fluorescence efficiency of anthracene dissolved in hexane and in ethyl alcohol, obtained by comparison with the scattering from a magnesium oxide surface as illustrated in Fig. 1.

Owing to the scattering of the incident light from the surface of the quartz cell and the blackened surround, and to the fluorescence of the quartz cell itself, the "blank" measurements in the above results, made by inserting a cell filled with a strong solution of potassium chromate, were of the order of 50 per cent. of the total readings. For this reason the efficiencies of the other hydrocarbons were determined by the relative method, illustrated in Fig. 2, taking the absolute efficiencies found for anthracene as the standard. The results are shown in Table II.

In the case of the weakly fluorescing substances in the above table the "blank" readings (obtained with the cell filled with solvent) could not be reduced below 75 per cent. of the total readings, and as the galvanometer

³ *J.A.C.S.*, 1931, 53, 3017.

TABLE I.

Wave-length A.	<i>In Hexane.</i>		<i>In Ethyl Alcohol.</i>	
	Concentration Gm./litre.	Percentage Fluorescence Efficiency.	Concentration Gm. litre.	Percentage Fluorescence Efficiency.
2540	0.012	14.8	0.6	21.8
—	—	16.4	—	21.8
—	0.13	15.9	—	21.5
—	—	14.4	—	22.9
—	—	14.6	—	—
—	0.97	14.2	—	—
2650	1.5	8.3	0.6	17.1
—	—	7.1	—	17.5
—	0.97	7.6	—	16.4
—	—	8.2	—	—
—	—	7.0	—	—
—	—	8.5	—	—
3135	1.5	7.95	0.6	18.2
—	—	7.35	—	17.5
—	—	7.0	—	16.2
—	0.97	7.2	—	—
—	—	7.9	—	—
—	—	8.1	—	—
3665	1.5	8.5	0.6	18.2
—	—	7.45	—	16.5
—	0.97	7.45	—	16.2
—	—	8.65	—	18.0
—	—	7.9	—	—

TABLE II.

SOLVENT, ETHYL ALCOHOL.

Solute.	Percentage Fluorescence Efficiency.			
	Concentration Gm./litre.	At 2650 A.	Concentration Gm./litre.	At 3135 A.
Benzene . . .	2.89	3.53	—	—
Naphthalene . . .	0.006	2.54	0.5	2.63
—	0.006	1.94	0.5	2.73
(Anthracene) . . .	0.05	17.0	0.05	17.3
Phenanthrene . . .	0.004	2.24	0.1	2.31
Triphenylmethane . . .	2.5	2.38	—	—
Fluorene . . .	0.01	35.7	0.5	16.6

zero was liable to change at the sensitivities necessary, a high accuracy cannot be claimed for the results.

Discussion.

The methods described above give under limits for the absolute fluorescence efficiencies, because in general the fluorescence and ab-

sorption bands of a substance overlap, and the fluorescence emitted is diminished in amount by absorption within the solution. Where the extinction coefficient of the incident light is large compared with the extinction coefficients of that part of the absorption band overlapped by the fluorescence band the error will be very small. This condition is fulfilled by anthracene at 2540 Å., and the results for that wave-length cannot be in error from this cause. There is good reason both theoretical and experimental² for expecting fluorescence efficiencies in simple cases to be independent of the wave-length of the exciting light, and the apparent drop in the values at the longer wave-lengths in the case of anthracene may be ascribed to the band overlap. If the extinction coefficient of the exciting light is of the same order as but not less than that of the average of the part of the absorption band overlapped by the fluorescence band the experimental results will be too low by amounts up to about one half of the true values. The results in Table II are subject to this consideration. They show clearly however the low efficiencies of benzene, naphthalene, phenanthrene, and triphenylmethane compared with anthracene and fluorene. The comparison between fluorene and triphenylmethane is interesting. Fluorene was given its name because of the intense fluorescence observed in its early preparations.⁴ It was later shown that the purified hydrocarbon showed scarcely any visible fluorescence.⁵ The present results show that its fluorescence is stronger than that of anthracene, though almost confined to the ultraviolet region, and very much stronger than that of triphenylmethane, whose appearance to the eye is deceptively powerful.

In order to obtain more accurate values for the hydrocarbons of Table II and others, it is intended to continue the work using a light source giving a more intense emission at 2540 Å. It is also proposed to investigate the quenching of fluorescence of hydrocarbons by added substances. As the process of quenching involves the removal of electronic energy and therefore requires marked interaction between the molecules it is hoped that such work will afford some information of the nature of the excited states of the hydrocarbon molecules.

Summary.

By means of a photo-cell combined with an "integrating screen," which provides a uniform wave-length sensitivity over the necessary range, the fluorescent efficiencies in the ultraviolet region of a number of simple hydrocarbons in hexane and ethyl alcohol solution have been measured.

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⁴ Berthelot, *Annales de chimie*, 1867, (4), 12, 222.

⁵ Fittig and Schmitz, *Annalen der Chemie*, 1878, 193, 134.

REVIEWS OF BOOKS.

Alchemy and other Chemical Achievements of the Ancient Orient.—

The Civilisation of Japan and China in Early Times as seen from the Chemical Point of View. By MASUMI CHIKASHIGE. (Tokyo : Rokakuho Uchida, 1936. Pp. vii + 102. Price 1.50 yen.)

The author, who is Emeritus Professor of Kyoto Imperial University, has based his work on a Japanese edition published six years ago. The translation, by Professor Sasaki, is in excellent English and the book is written in an attractive and scholarly style. It deals with ancient Chinese alchemy and its relation to alchemy in other lands, with bronze articles and the analyses of ancient Chinese bronzes, and with Japanese swords. The last section throws light on the metallurgical processes used by famous sword makers. The book is illustrated with several plates, one in colour, and is of considerable interest from the point of view of the history of Chemistry and Metallurgy.

J. R. P.

Alloys of Iron and Copper. By J. L. GREGG and B. N. DANILOFF.

(Pp. xii and 454. 30s. net.) **The Metal, Iron.** By H. E. CLEAVES and J. G. THOMPSON. (Pp. xii and 574. 36s. net.) McGraw-Hill Publishing Co. Ltd, London, 1935.

These two publications continue the series of monographs on Alloys of Iron which are being prepared by the Iron Alloys Committee of the Engineering Foundation under the able chairmanship of Dr. G. B. Waterhouse. They present critical summaries of published data bearing on the various alloy systems examined.

The effects produced by the addition of copper to iron or to steel have been commented on many times in the past, some of the statements made being misleading, to say the least. At one time, the presence of even small amounts of copper in steel was held to be highly detrimental, particularly to hot working properties. Nowadays, large tonnages of copper-bearing steels are regularly forged and rolled with perfect satisfaction.

The iron-copper alloys are interesting in many ways. The two metals alloy in all proportions by direct fusion, but at still higher temperatures, there is a miscibility gap which widens with increasing temperature. In the solid state, the metals form limited series of solid solutions. The extent of the liquid miscibility gap appears to be affected noticeably by impurities in the metal, particularly carbon, and the question has been raised as to whether, if absolutely pure metals were used, a miscibility gap would be formed.

Structural steels containing small amounts of copper are now being increasingly used on account of their greater resistance, as compared with ordinary carbon steels, to atmospheric corrosion, particularly in industrial areas. Copper is also useful in combination with small amounts of other alloys—chromium, molybdenum, manganese—in raising the tensile strength of certain structural steels without adversely affecting their ductility or workability to any notable extent. Such steels may contain up to about 0.5 per cent. copper ; when larger amounts are added,

e.g., 1.0/1.5 per cent., interesting precipitation hardening effects may be produced, though it is doubtful at present whether they have any economic value. An account of all these materials, and also of the effects of copper additions on the properties of cast irons and corrosion-resisting steels are given by the authors, with that completeness of detail which is a feature of this series of monographs.

The other volume deals with the attempts which have been made to produce iron as free as possible from all impurities, and with the properties of these high purified metals. As the authors state, perfectly pure iron has never been prepared, at least in useful quantities; consequently its properties, which should be the basis of investigations on the effects of alloys on iron, have never been determined. Iron of a very high degree of purity has, however, been produced in appreciable quantities, and the authors summarise very clearly the changes in properties which occur as the content of impurity is reduced. Perhaps the most interesting effects are produced on magnetic properties, but here the subject is complicated by the fact that much depends on the type of impurity as well as the amount. Thus, it has been shown that hydrogen-treated ingot iron may have magnetic properties far superior to those of annealed electrolytic iron of greater purity.

Much has been said in the past regarding the effect of impurities on the corrodibility of iron, and it has been frequently considered that pure iron would be relatively resistant to corrosion. It seems likely, however, that the effect of purity, as between very pure irons and commercial products, is usually less important than that of environment. Iron, even when pure, is not inherently resistant to corrosion; real resistance is only obtained by incorporating substantial amounts of other elements, *e.g.*, silicon, chromium, nickel, which modify appreciably the characteristics of the oxide film which, as Evans has shown, is produced on the surface of iron by contact with the atmosphere.

The authors give a very complete account of the various methods used in preparing iron of high purity and of the properties of the materials so produced; their book is a veritable storehouse of all the relevant information on these important subjects.

Metallurgists owe a debt of gratitude to the Engineering Foundation for financing the production of these very useful volumes, and to the Committee, who are responsible for their preparation, for the great care they take to ensure that the accounts given of each alloy system are as complete and accurate as the wit of man can devise. The series of volumes should be in every metallurgist's library.

The Organic Chemistry of Nitrogen. By N. V. SIDGWICK. New Edition revised and rewritten by T. W. J. TAYLOR and W. BAKER. Oxford: Clarendon Press, and London: Humphrey Milford, 1937. Pp. xix + 590. Price 25s. net.

The first edition of this book, published in 1910, has long been out of print and scarce, and the appearance of a new and completely revised edition is an event which will be greeted with satisfaction. The original edition was characterised by certain special and very attractive features, and these are again prominent in the new edition. Although written from

the point of view of organic chemists, and with satisfactory emphasis on the methods of preparation and reactions of the substances concerned, the book achieves a successful relation of descriptive material to fields of general theory and with the physico-chemical aspects of the whole subject.

The field of materials covered is really very extensive, although the purine derivatives and simple alkaloids have been omitted from this edition. The treatment is clear and closely related to experiment, so that the reader does not feel that he is lost in the complexities of the subject. It is obviously impossible to give an adequate account of the contents of the eighteen chapters of the book, but it may perhaps be mentioned that some of them contain material of great interest to bio-chemists, whilst the accounts of the diazo-compounds, azoxy- and azo-compounds, and the five- and six-membered rings will probably be of special interest to organic chemists. The printing and paper are excellent and the price is very moderate.

Thorpe's Dictionary of Applied Chemistry. Fourth Edition (vol. I., A-Bi). By J. F. THORPE and M. A. WHITELEY. (London: Longmans, Green & Co. Pp. xxvii and 703.) Price 3 guineas net.

Thorpe has been one of the most used books in the reviewer's library for many years. Less than two years ago the last volume of the Supplement to the third edition appeared, and it was scarcely to be hoped that, so soon, the editors would recommence their herculean task. The fourth edition is, however, under way and greatly will it be welcomed. Thorpe continues to grow; the new volume occupies forty more pages than were devoted to similar entries in the last edition with its supplement, the article on "Analysis" being presumably rechristened "Chemical Analysis" and left for a later volume.

The compilers have taken the wise step of building anew. This volume is rewritten almost in its entirety; in a few cases only, *viz.* the introductions to some of the articles, is the text taken from earlier editions. The general plan of the last edition is followed, however, and each entry consists of a monograph written by an acknowledged expert. Every year we may expect a new volume, until the task is completed; in order that the earlier volumes may be kept up-to-date, appropriate cross references in later volumes will be utilised to introduce the later acquired knowledge. This is admirable—as far as it goes—and is probably the only way in which such a series of volumes can be kept reasonably up to date, but it has the obvious weakness that only a few entries in vols. I. to IV. or so can hope to find relevant cross-entry under W, X, Y, Z. We may perhaps be permitted to wish the editors and their colleagues more power to their elbows and may all their years be little ones!

A detailed review of such a work is obviously impossible. Suffice it to say that the reviewer has spent many more hours than he intended in reading it and that he looks forward eagerly to the appearance of the next volume. If there be any who do not know Thorpe, it may be said that the word "Applied" in the title is of historical rather than real present significance. The fact that seven and a half pages are devoted to an article on "atomic structure" is sufficient indication that the monographs are very far from being confined to subjects only of industrial interest; where,

however, a subject involves industrial considerations, that interest is adequately dealt with. We have here, in fact, an alphabetically arranged series of monographs which will, as a rule, be readily understandable by any ordinarily cultured reader.

Applied Radiochemistry. BY O. HAHN. (New York: Ithaca. Pp. xi and 278. Oxford University Press. Price 11s. 6d. 1936.)

This volume contains the substance of lectures delivered by the author as Non-Resident Lecturer at Cornell in 1933. Their field is wider than the title suggests: actually only part III and IV deal with "applied" radiochemistry in the usual sense, and more than the first half of the book is devoted to attempts at a theoretical systematisation of the chemical behaviour of the radioelements. But in so far as the rules found for them must hold good also for other elements present only in imponderable amounts, their study may be rightly said to be "applied" radioactivity. The book mainly embraces researches carried out under the author's guidance in the Kaiser Wilhelm Institute for Chemistry in Berlin-Dahlem; both their high value and their somewhat intricate nature will certainly make the collection very welcome to all chemists interested in radioactivity.

No less than 100 pages of part II are occupied by a discussion of the "Separation of Minute Amounts of Material when Macroscopic Precipitates are formed" and of the "Deposition of Minimal Amounts of Material upon Preformed Precipitates"; or, in other words, they deal with "Hahn's Precipitation and Adsorption Law." The author invariably calls the rules formulated by him "laws," while these postulated by earlier investigators are named "rules"; but this is only a terminological peculiarity without any deeper claim, as he himself points out that his "laws" have not the general applicability originally expected of them; and he further discusses fully the exceptions so far established. No analytical chemist will be astonished to hear that there are too many relevant factors (the solubilities of the two substances in question; the presence, or absence, of isomorphism, or isodimorphism; the area, and the electric charge, of the surface of the precipitate) to allow of the formulation of a strict law expressed in a short sentence; but all will agree that the extensive researches of the author and his co-workers have helped greatly to the clarification of these theoretically and practically important questions.

The contents of the later parts of the book are likewise too rich for more than a few indications to be given here. One of the most useful practical results of the author's studies on the emanating power of various gels containing radium salts is certainly the development of a device for obtaining highly concentrated radon from "dry preparations." If, as usual, the aqueous solution of a radium salt is used as a source, the purification of the radon from H_2 , O_2 , H_2O and CO_2 is rather a troublesome process; but if, on the other hand, one of Hahn's "dry preparations" (e.g., $Fe(OH)_3$, containing $RaCO_3$, and freed from water by means of ethyl alcohol and ether) serves as a radon source, a very simple apparatus (containing, besides a few valves and a storage vessel, only an annexe filled with calcium filings and a spiral dipped in liquid air) makes it possible to obtain up to 85 per cent. of the equilibrium amount of radon in great purity.

There are many other interesting chapters in the book. Its author

has devoted more time than anyone else now living to the study of radio-chemical problems. To possess some of his recent researches in such a well printed and excellently illustrated volume will be an inspiration to all others working in similar fields.

F. A. P.

Atomic Structure of Minerals. By W. L. BRAGG. (London: Humphrey Milford, Oxford University Press, 1937. Pp. xiii and 292. Price 18s. net.)

The George Fisher Baker Non-resident Lectureship at Cornell has been the means of publishing a number of books on various branches of chemistry. The present volume is a little removed from the ordinary in that it does not correspond to the author's course, but has been written as a contribution to the literature of that branch of crystallography which Professor W. L. Bragg has made particularly his own—the structure of inorganic substances.

The book falls into two distinct portions, the necessary parts of structural analysis, and a detailed account of mineral structures. It is most valuable to have so complete a discussion of the labours of the Manchester School and a conspectus of work all the world over in such a readable form. Full recognition is given to the difficulty of becoming proficient at "thinking in three dimensions"; nevertheless, the diagrams reproduced are sufficiently numerous, as well as excellent, to help a great deal in acquiring the necessary skill. The reader is urged to prepare models for himself. This is a fascinating occupation, and one in which students can now indulge at a comparatively early stage in their career. It is interesting to notice how great is the debt which these modern developments owe to the methods of classical crystallography. Continuity has not been lost in passing from external form to internal arrangement.

A few points may be selected to show how wide, and yet at the same time how detailed a view these pages provide. The usual classification of forces (ionic, homopolar, metallic, van der Waals) is accepted as convenient, but having in itself no profound significance: the systems of nuclei and electrons are subject ultimately to minimal energy conditions alone, and thus "class distinctions" disappear. In this connection, it is salutary to recollect that the rigid expression for the heat of formation of rocksalt from separated sodium and chlorine atoms has not yet been obtained; a useful caution against overlooking the limitations of simplified concepts.

A word or two must be added about the photomicrographs of orientated crystals upon mica (Plate VIII.). The subtlety and delicacy of this phenomenon are entrancing, as well as the analogous effect when an anisotropic melt is introduced between a couple of mica cleavage plates. This causes the optic axes of the melt to swing round, and demonstrates the presence of a glide plane, as opposed to a symmetry plane, in such a crystal.

Professor Bragg has brought system and order into what is otherwise a bewildering array of substances, and in the course of so doing has produced a book which many will desire to possess.

F. I. G. R.

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THE DIFFRACTION OF ELECTRONS BY CADMIUM IODIDE.

BY G. I. FINCH AND H. WILMAN.

Received 24th May, 1937.

1. Introduction.

The phenomena peculiar to the diffraction of fast electrons by exceptionally thin single crystal films have previously been studied with graphite¹ and molybdenite.² These have relatively simple layer-lattice structures and can be obtained in very thin single-crystal sheets by careful cleavage from good natural crystals. The thinnest crystal flakes obtained from these minerals were translucent and practically colourless, and yielded brilliant and extensive electron diffraction patterns consisting either of spots in simple two-dimensional array when the crystal was undistorted and stationary, or of prominent and continuous diffraction lines if the flake had been bent during cleavage or was undistorted but rotated during exposure of the photographic plate. In a rotation pattern from a cross-grating plane of one atom thickness each diffraction line should vary gradually in intensity throughout its length. Wherever the lines recorded in patterns from the stationary bent or rotated undistorted crystal films crossed the normal Hull-Debye-Scherrer ring positions, however, they always showed regions of greatly increased intensity corresponding to normal diffraction spots of three-dimensional origin, although otherwise they exhibited the characteristics of a true cross-grating effect; thus the lines occurred mostly in pairs symmetrically disposed with respect to the central undeflected spot. It is clear, therefore, that even the thinnest crystal flakes examined must have been at least two or three molecular layers thick.

Besides the more prominent diffraction spots, which were normal in that their positions fitted in with the crystal structure as determined by X-rays with large crystals, many other more or less strong "extra" diffraction spots were observed on the two-dimensional lines, but were particularly clear and sharp on similar lines of lesser intensity recorded in patterns approaching the random Hull-Debye-Scherrer type which had been obtained from more or less torn or crinkled single-crystal films. Measurement of the radial distances of a large number of such spots from the undeflected spot showed that these were not in any way haphazard, but that each distance was representative of at least several diffraction spots within the limits of error of each measurement (about 2°/100); further, these radii were found to agree very closely with the interpretation of the "extra" spots as diffractions which either had integral indices, but were "forbidden" by the structure factor of the

¹ G. I. Finch and H. Wilman, *Proc. Roy. Soc., A*, 1936, **155**, 345.

² G. I. Finch and H. Wilman, *Trans. Faraday Soc.*, 1936, **32**, 1539.

atomic arrangement, or had a fractional third index relating to the hexagonal axis which is normal to the cleavage (001) plane of graphite and molybdenite.* On the other hand, the "extra" diffractions appear to be quite incompatible with effects which could be caused by (i) impurities in the mineral samples chosen, (ii) grease layers occurring adventitiously on the crystal surfaces, (iii) lattice dimensional changes near the crystal boundary, or (iv) the slipping during cleavage of layer planes over one another into stable though crystallographically abnormal positions.²

Though "extra" diffractions normally forbidden by structure factor are now well known to be capable of formation as a result of multiple scattering of the electrons in the crystal,³ the other class of anomalous diffractions could not be produced in this way. In the case of graphite, where the above effects were first noted,¹ the Kikuchi line patterns from thicker films were found to be in complete agreement with the structure as determined by X-rays. With thin molybdenite and mica² it was also clearly shown that the continuous diffraction lines joining up families of normal diffractions and the intermediate "extra" diffractions lying on these lines became fainter with increasing crystal thickness until, finally, only normal stationary or rotation spot patterns of three-dimensional type were obtained. The diffraction lines and "extra" diffractions are thus due to the greatly increased tolerance in the third Laue condition for diffraction by the crystal, as a result of the exceptional thinness of the flakes examined.

In what follows an account is given of a further experimental test of the theory of the origin of the "extra" diffractions yielded by thin layer-lattice crystals, consisting in a study of the diffraction of electrons by cadmium iodide, which is another pure anhydrous material of layer-lattice structure and readily obtained in the form of thin crystalline films. Additional interest is provided here by the fact that the specimens used were prepared directly by a building-up process instead of by cleavage.

2. The Structure of Cadmium Iodide.

X-ray diffraction patterns of cadmium iodide were first obtained by Bozorth⁴ from light-yellow hexagonal tabular crystals grown from solution. Line spectra from (001), (100) and (110) faces, and Laue photographs with the beam either normal or inclined to the (001) plane indicated that the unit cell was hexagonal with $a = 4.24$ Å., $c = 6.84$ Å., $c/a = 1.613$, and contained one molecule of CdI_2 , since the density was 5.644. From the fact that the symmetry of the Laue photographs was trigonal and from the relative intensities of the $h00$ and of the $00l$ diffractions Bozorth attributed to the cadmium and iodine atoms the positions $(00\frac{1}{2})$ and $(\frac{1}{3}\frac{2}{3}u)$, $(\frac{2}{3}\frac{1}{3}\bar{u})$ respectively, where $u \approx 0.25$. These atom positions correspond to a molecular layer structure, each layer consisting of two plane hexagonal networks of iodine atoms so superposed that the atoms of one rest on those of the other in alternate inter-

* The considerable number of "extra" diffractions lying within the 100° ring in the molybdenite patterns, however, remain unexplained.

² F. Kirchner, *Z. Physik*, 1932, **76**, 576; H. Raether, *Z. Physik*, 1932, **78**, 527; R. Beeching, *Phil. Mag.*, 1935, **20**, 841; G. I. Finch and C. H. Sun, *Trans. Faraday Soc.*, 1936, **32**, 832; see also H. Bethe, *Ann. Physik*, 1928, **87**, 55; and J. W. Harding, *Phil. Mag.*, 1937, **23**, 271.

⁴ R. M. Bozorth, *J. Amer. Chem. Soc.*, 1922, **44**, 2232.

stices, with a similar network of cadmium atoms sandwiched midway between the two in such a manner that each cadmium atom lies at the centre of a line perpendicular to the layer plane and joining the centres of two triangles of iodine atoms. Such layers are superposed in contact with the same orientation, and so that the cadmium atoms of one layer are directly above those of the next below, the iodine atoms being in contact in a hexagonal close-packed formation.

Later, however, Arnfelt⁵ reported having obtained X-ray powder photographs from cadmium iodide in which the presence of additional lines suggested that Bozorth's c axis value should be doubled. Hassel⁶ stated that he had been able to confirm this by Laue, rotation and Bragg-reflection photographs (which were not reproduced or described) from crystals grown from aqueous solution at room temperature, which appeared good but never actually gave clear Laue patterns, although the rotation diagrams were very sharp and gave the values $a = 4.24$ Å. and $c = 13.67$ Å. Hassel redetermined the atom positions from the intensities (not stated) of the diffractions in the rotation diagrams as 2 Cd at (000), ($\frac{1}{3}\frac{2}{3}\frac{1}{2}$) and 4 I at ($\frac{2}{3}\frac{1}{3}\bar{u}$) ($\frac{1}{3}\frac{2}{3}u$), ($00\frac{1}{2}+u$), ($\frac{2}{3}\frac{1}{3}\frac{1}{2}-u$) where $u \approx \frac{1}{8}$. This corresponds to a layer structure in which the layers are exactly like those in the structure formerly proposed by Bozorth, but with alternate layers rotated through 60° about the vertical line through the point ($\frac{2}{3}\frac{1}{3}0$).

Electron diffraction patterns have been obtained from vaporised polycrystalline cadmium iodide films by Kirchner,⁷ who showed that very thin cadmium iodide films, condensed *in vacuo* on to collodion, when freshly formed gave patterns of broad rings with the beam normal to the supporting film, but that crystal growth occurred even at room temperature, since the diffraction rings were seen to become sharper, and after one night had broken up into arcs. Thicker films exhibited pronounced (001) orientation and yielded ring patterns comprising mainly strong hko diffractions when normal to the beam; on inclination, the pattern developed into families of hkl arcs such that the arcs of each group lay across the circumference of elliptic loci whose eccentricity increased with the inclination of the film to the beam. More or less continuous diffuse regions along the circumference of these ellipses were ascribed by Kirchner to the extreme thinness in the c -axial direction of some of the orientated crystal flakes, which therefore behaved almost like pure cross-grating layers to give continuous (hk) diffraction ellipses. Kirchner concluded that the net-plane spacings calculated from the radii of the rings obtained from the larger crystals agreed with those calculated from Bozorth's structure, and ascribed the somewhat lower values obtained from the diffuse rings yielded by the thinner films to a one-sided broadening of the rings as a result of the extreme thinness of the crystals.

Thus there is some doubt as to the structure of CdI_2 , and until this is settled it is not possible to say which of the diffractions recorded below are anomalous.

3. Experimental.

Specimens were prepared from crystallised cadmium iodide supplied by Hopkins and Williams, (i) by condensation *in vacuo* on to a cool thin

⁵ H. Arnfelt, *Arkiv. f. Mat., Astron., Fysik*, B, 1932, **23**, No. 2.

⁶ O. Hassel, *Z. physik. Chem.*, 1933, **22**, 333.

⁷ F. Kirchner, *Z. Physik*, 1932, **76**, 576.

collodion substrate supported on nickel gauze, and (ii) by evaporation of a solution in water or alcohol, or a mixture of the two, either upon a thin collodion substrate mounted on nickel gauze, or in the meshes of the gauze alone to form films bridging the interstices. The specimens formed by condensation from the vapour had the appearance of a white powder, yellowish by transmitted light, whereas those crystallised from solution were more glistening and transparent though also partly opaque-white. Electron diffraction transmission patterns were recorded from various parts of about twenty specimens prepared as above, using Camera No. 2 (Cambridge), the accelerating potential being about 50 KV and camera length 50 cms. throughout, except for Fig. 12, where it was about 22 cms.

4. Results.

(i) Specimens Prepared from Solution.

(a) Polycrystalline specimens prepared by rapid evaporation of the solution in the meshes of a nickel gauze *in vacuo* gave electron diffraction patterns of rings, Fig. 1, which did not show any signs of arcing or intensity changes on inclination of the specimen to the beam. This type of pattern is therefore characteristic of cadmium iodide crystals in random arrangement. Owing to the presence of banded regions similar to those observed in patterns from random polycrystalline graphite¹ and mica² (e.g. from the 100 ring outwards) and of the considerable amount of background intensity usually present in these patterns, the accuracy of measurements obtained from such patterns was not high, hence none were used for purposes other than comparison with the patterns obtained by other methods.

(b) On the other hand, specimens prepared by evaporation of the solution on thin collodion films *in vacuo* generally yielded brilliant ring patterns, such as Fig. 2, when the specimen plane was perpendicular to the electron beam, and on inclination of the specimen these rings broke up into arcs, and new arcs appeared, as shown in Figs. 3 and 4, taken at about 27° and 62° inclination from the normal setting respectively. The circular arcs form groups which lie on the more or less strong elliptic bands noted by Kirchner,⁷ which have their centres in the undeflected spot and their major axes perpendicular to the projection of the axis of inclination upon the plate. From measurements of ring patterns, such as Fig. 2, it was found that these rings corresponded to the *hko* diffractions of the cadmium iodide hexagonal lattice, while the arcs of other rings appearing on inclination of the specimen were *hkl* diffractions; thus the crystal particles had grown up in strong orientation with their basal (001) planes parallel to the collodion substrate. These patterns of arcs from an orientated polycrystalline specimen correspond closely to the well-known single crystal "rotation" type of photograph in X-ray technique, although the primary beam is not perpendicular to, but inclined at an angle, θ , to the "rotation," i.e. in electron diffraction the "orientation," axis.* Thus in the present case, where the orientation axis is [001], the arcs fall into groups with the *l*-index equal to 0, 1, 2, 3, etc., occurring respectively where the zero, 1st, 2nd, 3rd, etc., order layer lines from the central spot cross the corresponding *hkl* Hull-Debye-Scherrer ring positions.† The layer lines in these patterns are the intersections of the photographic plate with the diffraction cones round the lattice rows parallel to the orientation axis; thus they are practically equidistant straight lines in the case of the small angles of deviation concerned here, with spacing equal to $\frac{\lambda L}{c \cos \theta}$

* G. I. Finch, A. G. Quarrell and H. Wilman, *Trans. Faraday Soc.*, 1935, **31**, 1050.

† Sometimes also called "fibre" axis.

† This method of determining the theoretical arc positions is also the simplest for reflection patterns from orientated polycrystalline specimens.

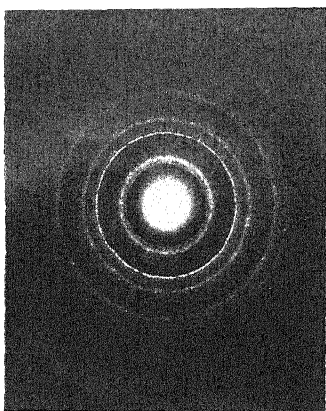


FIG. 1.—Random CdI_2 crystals.

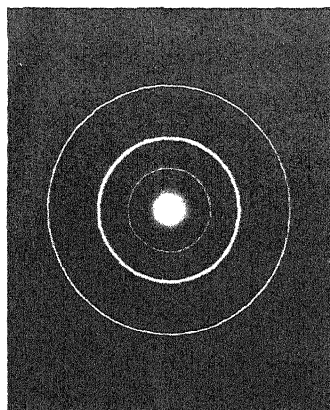


FIG. 2.—(001) orientation; beam $[001]$.

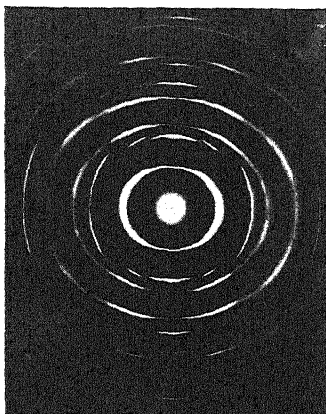


FIG. 3.—(001) orientation; $\theta = 27^\circ$.

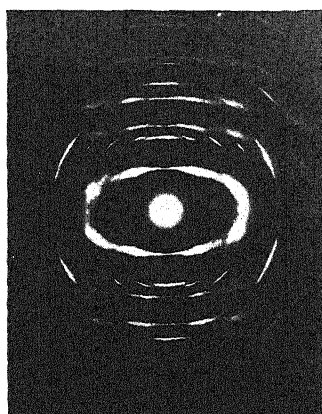


FIG. 4.—(001) orientation; $\theta = 62^\circ$.

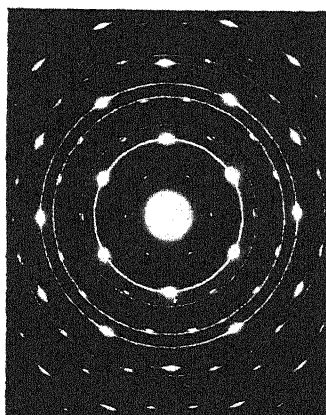


FIG. 5.—Single crystal (mosaic) in a polycrystalline film of (001) orientation; beam $[001]$, i.e., $\theta = 0^\circ$.

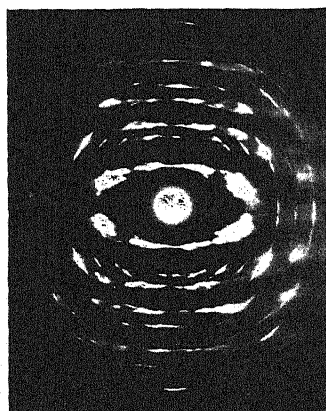


FIG. 6.—Specimen similar to Fig. 5, but $\theta = 63^\circ$.

[To face page 1438.]

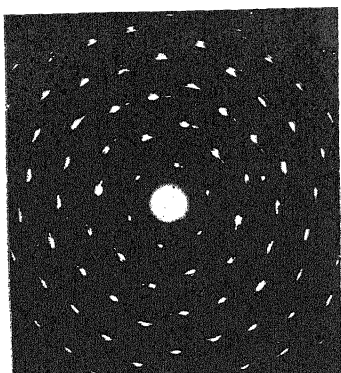


FIG. 7.—Imperfect single crystal ;
 $\theta = 0^\circ$.

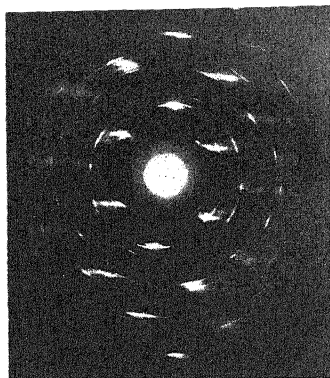


FIG. 8.—Specimen of Fig. 7 inclined,
 $\theta = 32^\circ$.

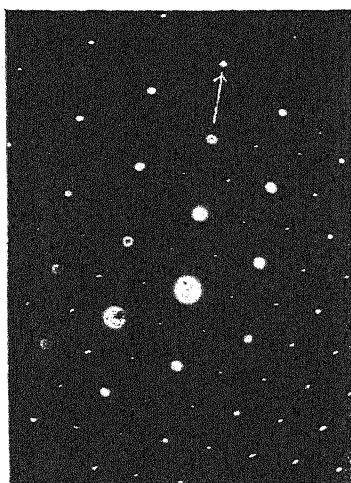


FIG. 9.—Nearly perfect single crystal ;

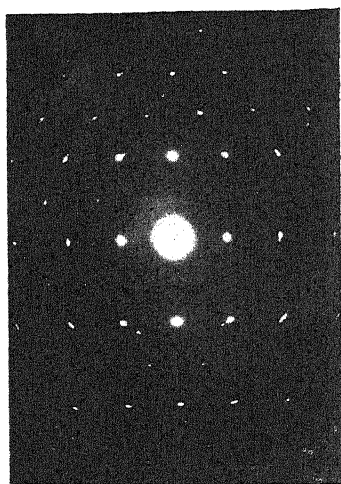


FIG. 10.—Specimen of Fig. 9 inclined,
 $\theta = 25^\circ$.

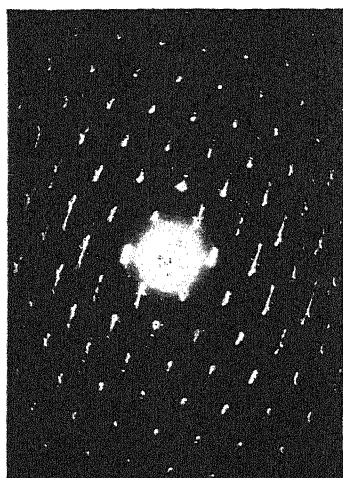


FIG. 11.—Very thin specimen ; crystal curvature producing streaks.

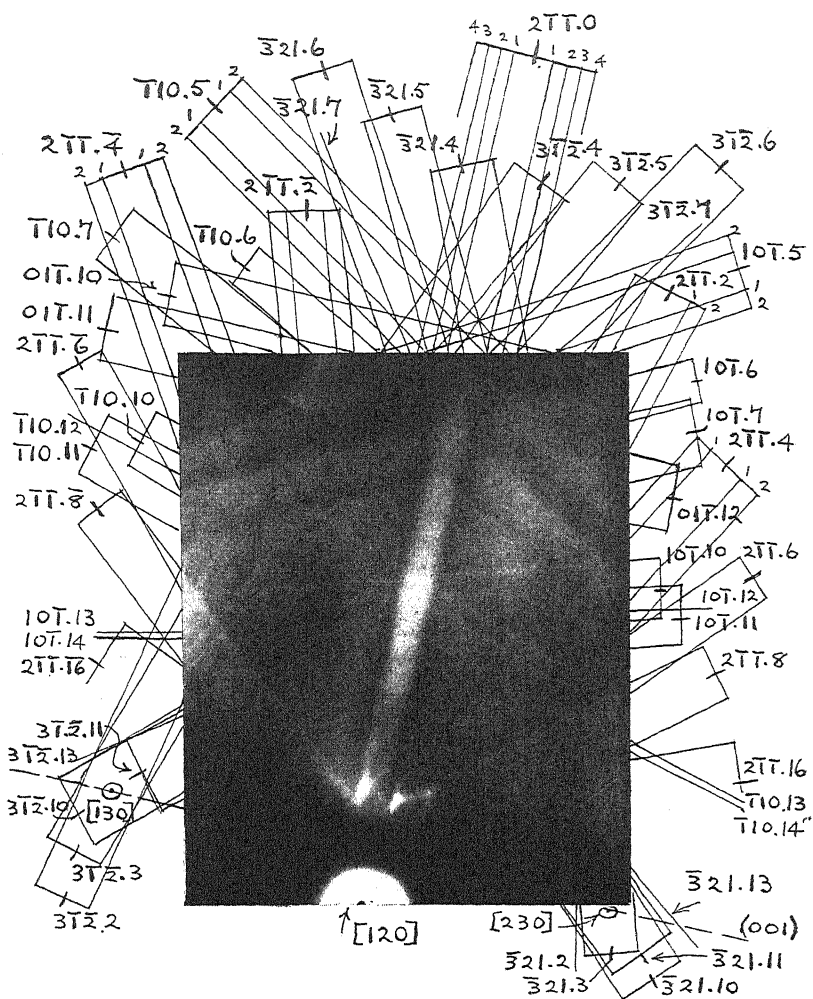


FIG. 12.—Reflection from (001) face of a CdI_2 crystal grown from solution.

[See page 1442.]

as shown in Fig. 4a. The arcs on each elliptic locus of the pattern can also be conveniently grouped together, since all diffraction arcs on a given ellipse have the same (hk) indices but different l indices. If all the orientated crystal flakes were only one atom thick, *i.e.* pure cross-grating sheets of atoms, the pattern would consist of the continuous ellipses alone, whose minor axes are the corresponding hko Hull-Debye-Scherrer ring radii and whose major axes are equal to $1/\cos \theta$ times the respective minor axes, where θ is the angle of inclination from the setting in which the orientation axis is parallel to the beam. From the fact that the elliptic bands are sharp near the ends of their minor axes and broad near the ends of their major axes, we can conclude that the thin crystal sheets giving rise to the bands are of large extent in the (001) plane and orientated parallel to the substrate film, but that the latter is slightly curved between the meshes of the supporting gauze.

As already stated, the random patterns like Fig. 1 were unsuitable for accurate measurement, but the main arcs in the patterns from strongly inclined specimens were sharp and clear, so that the measurements of diameters agreed closely with each other. A typical set of spacings calculated from their diameters based on the X-ray value of $a = 4.240 \text{ \AA.}$ are given in Table I, and show that, in

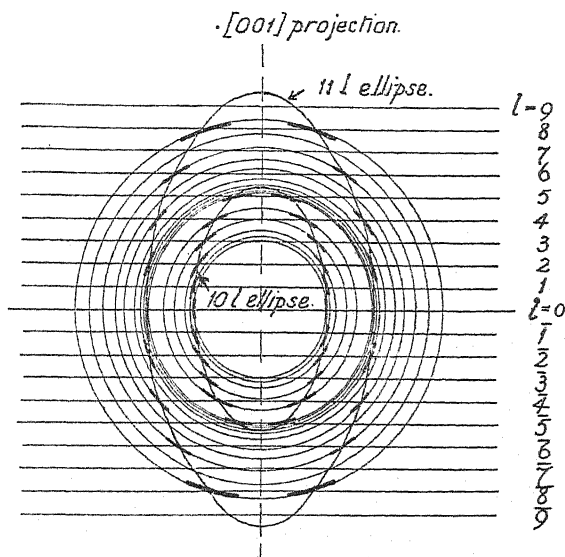


FIG. 4a.—Approximate arcing positions of the $10l$ and $11l$ diffractions for $\theta = 50^\circ$, the crystal orientation being (001).

addition to those arcs of the pattern which were to be expected from Bozorth's structure, several moderately strong and well-defined arcs were present which would only correspond to integral indices if an axial ratio approximately equal to that postulated by Arnfelt and Hassel was assumed. This axial ratio was therefore, for the time being, assumed to be the correct one, and the diffractions were indexed accordingly. Besides the more clearly marked additional arcs just described and to which integral indices have been assigned in Table I, there were, however, signs of a few fainter intermediate arcs lying on the same loci in the region of the elliptic bands; owing to their more diffuse nature and the presence of the banded regions underlying them these arcs were not clear enough to be measured with much accuracy and are accordingly not included in Table I, but they appeared to correspond to diffractions with integral h and k indices but fairly simple fractional l values.

Most of the specimens evaporated from solution on collodion contained regions which yielded electron diffraction patterns, even when perpendicular to the beam, in which the hko rings mainly composing the pattern were more or less strengthened by arcs or spots (Fig. 5). When such spot and ring patterns were present simultaneously in the photograph the

strong spots lay within the breadth of the rings as far as could be determined. Parts of the specimen from which arced or spotted patterns similar to Fig. 5 were obtained at normal transmission yielded on inclination

TABLE I.—ANALYSIS OF THE ARC PATTERN OF FIG. 4

d in Å. Referred to $a = 4.240$ Å.	Indices of the Diffractions Assuming $c/a \approx 3.226$.	d in Å. Calculated for $a = 4.240$ Å., $c/a = 3.226$.
3.689	100	3.672
3.558	101	3.546
3.227	102	3.236
2.852	103	2.859
2.486	104	2.502
2.181	105	2.194
2.123	110	2.120
2.028	112	2.024
1.938	106	1.937
1.835	200	1.836
1.813	201	1.819
1.800	114	1.802
1.765	202	1.773
1.701	203	1.703
1.617	204	1.618
1.552	116	1.553
1.500	205	1.525
1.426	206	1.430
1.386	120	1.388
1.353	122	1.361
1.331	118	1.331
1.328	123	1.328
1.275	124	1.288
1.253	208	1.251
1.231	125	1.238
1.223	300	1.224
1.199	302	1.205
1.185	126	1.187
1.174	303	1.182
1.152	11.10	1.149
1.149	304	1.152
1.075	306	1.078
1.060	220	1.060
1.046	222	1.047
1.017	130	1.018
1.003	11.12	1.004
1.001	132	1.007
0.993	308	0.996
0.990	133	0.994
0.970	134	0.976
0.954	135	0.960
0.928	136	0.930
0.918	400	0.918
0.899	137	0.907
0.841	230	0.842
0.802	140	0.801

tion patterns of arcs with a non-uniform intensity distribution along their length, Fig. 6, and the bands joining up the arcs of each group of diffractions were also made up of irregular regions of diffracted intensity, being sometimes diffusely patchy and in other cases having quite a fine granular appearance as though made up of diffraction spots of varied sharpness and intensity.

Several parts of thin specimens were met with, yielding patterns of blurred patches with superposed short arcs in approximately a regular hexagonal arrangement, Fig. 7, at normal incidence, but which gave on inclination patterns, such as Fig. 8, consisting of more extensive blurred streaks with superposed arcs where they crossed the Debye-Scherrer ring positions. Fig. 8 corresponds roughly to the pattern obtained at normal incidence (Fig. 7) elongated in a direction at right angles to the axis of inclination in the ratio $1/\cos \theta : 1$, where θ is the angle of inclination from the normal setting; but the elongated appearance of the streaks shows that Fig. 8 is analogous to the pattern obtained by rotation (or bending) of a very thin single crystal film through a considerable angular range.² Thus the corresponding region of the specimen must have consisted of many small flakes with nearly the same orientation with respect to the substrate, approximating to a single crystal with very crude mosaic structure with an approximately uniaxially curved shape.

Well-defined spot patterns were often obtained alone or superposed on Hull-Debye-Scherrer rings. Fig. 9 shows the regular hexagonal pattern of the hko diffractions obtained with the beam normal to the specimen plane. The diffraction spots fall into two groups,

those with $(h + 2k) = 3p$ where p may be 0, 1, 2, 3, etc., being stronger than the rest, while the spots of each group have practically uniform intensity, apart from the continuous radial decrease. On inclination of the specimen through 25° about the axis parallel to the arrow in Fig. 9 the pattern shape was elongated correspondingly, Fig. 10, while the spot intensities were again systematically strong or weak.

Besides the spot patterns of the above types, several were obtained from inclined specimens which showed almost uniform and only medium intensity of the rather sharp spots in not quite regular hexagonal array. Faint diffuse lines were more or less clearly visible in several spot patterns along the spot rows parallel to the sides of the hexagon unit of the pattern. Similar lines have previously been observed by Cochrane (electrodeposited metal single crystals),⁹ by Storks and Germer (stearic acid)¹⁰ and in this laboratory in patterns from mica, graphite, anthracene, phthalimide and from thin long-chain hydrocarbon-compound crystals.¹⁴

Several patterns similar in type to Fig. 11 were obtained in which a constellation of closely spaced fine spots occurred instead of each single spot of the simple hexagonal pattern, and sometimes these constellations approximated to blurred areas. Five patterns showed such groups of spots occurring in simple linear groupings superposed on more or less intense streaks such as were obtained from graphite¹ and molybdenite,² and Fig. 11 shows these features as clearly as it is possible to reproduce such fine detail. Measurements of the radial distances of a large number of these spots indicated, as in the case of graphite and molybdenite, that the spots were not haphazard while, indeed, when several streaks occurred side by side, as in Fig. 11, the main spots lying on them were often seen to fall at the same radial distances from the central spot, exactly as was noted with the molybdenite "extra" diffractions. The spots,

TABLE II.

Observed d in A. Referred to $d_{110} = 2.120$ A.	1-Indexing on the Basis of $a = 4.240$ A., $c/a = 3.226$.	d Calculated, A.
A. Measurements of 10ℓ Diffractions on the Corresponding Streaks in Fig. 11.		
3.674	0	3.672
3.638	1/2	3.639
3.616	2/3 ; 3/5 ; 5/7	3.612 ; 3.624 ; 3.606
3.596	4/5 ; 3/4	3.589 ; 3.599
3.572	6/7 ; 8/9	3.577 ; 3.571
3.547	1	3.546
3.523	8/7 ; 10/9	3.510 ; 3.519
3.485	5/4	3.482
3.470	9/7	3.471
3.438	10/7 ; 7/5	3.429 ; 3.436
3.418	10/7	3.429
3.406	3/2	3.406
3.372	8/5	3.373
3.351	5/3	3.353
3.331	12/7	3.335
3.323	7/4	3.323
3.291	16/9 ; 11/6	3.299 ; 3.295
3.277	13/7	3.286
3.263	?	—
3.214	10/2 ?	3.236
3.207	?	—
3.154	9/4 ; 11/5	3.144 ; 3.163
3.123	16/7	3.130
3.111	7/3	3.112
3.069	22/9 ; 17/7	3.069 ; 3.076
3.045	5/2	3.049
3.007	13/5	3.015
2.975	8/3 ; 19/7	2.985 ; 2.968
2.948	11/4	2.955
2.919	20/7 ; 17/6	2.912 ; 2.922
2.902	26/9	2.901
2.866	3	2.859
2.845	?	—
2.820	28/9	2.818
2.807	22/7 ; 17/5	2.806 ; 2.806
2.758	13/4 ; 23/7	2.767 ; 2.754
2.726	10/3	2.736
2.683	7/2	2.676
2.653	25/7	2.652
2.611	11/3	2.617
2.583	15/4	2.588
2.566	19/5 ; 23/6	2.572 ; 2.559
2.524	?	—
2.498	4	2.502

⁹ W. Cochrane, *Proc. Phys. Soc.*, 1936, 48, 723.

¹⁰ K. H. Storks and L. H. Germer, *J. Chem. Physics*, 1937, 5, 131.

TABLE II.—(Continued).

Observed d in Å. Referred to $d_{110} = 2.120$ Å.	l -Indexing on the Basis of $a = 4.240$ Å., $c/a = 3.226$.	d Calculated, Å.
2.120	0	2.120
2.080	4/3; 6/5; 5/4	2.076; 2.084; 2.081
2.060	3/2; 10/8; 14/9	2.065; 2.058; 2.061
2.031	2	2.024
1.997	7/3; 16/7; 9/4; 20/9	1.994; 1.998; 2.002; 2.000
1.987	12/5; 22/9	1.987; 1.982
1.967	5/2; 13/5	1.976; 1.968
1.963	8/3; 13/5	1.959; 1.968
1.953	11/4	1.950
1.945	14/5	1.945
1.927	3; 20/7	1.922; 1.929
1.902	16/5; 22/7	1.899; 1.905
1.883	10/3	1.884
1.873	24/7	1.872
1.861	7/2	1.864
1.855	18/5	1.852
1.840	11/3; 26/7	1.843; 1.837
1.831	15/4; 34/9	1.833; 1.830
1.820	19/5; 23/6	1.827; 1.823
1.801	4	1.802
1.782	21/5	1.777
1.772	30/7; 17/4; 38/9	1.766; 1.770; 1.774
1.759	13/3	1.761
1.746	9/2; 22/5	1.739; 1.751
1.733	32/7; 40/9	1.730; 1.735
1.714	14/3; 19/4; 23/5	1.717; 1.707; 1.708;
1.696	24/5; 34/7; 44/9	1.701; 1.694; 1.690
1.681	5	1.676
1.663	36/7; 46/9	1.658; 1.662
1.648	26/5; 21/4	1.651; 1.644
1.635	16/3	1.634
1.630	27/5	1.626
1.618	38/7	1.622
1.614	11/2	1.614
1.601	28/5; 50/9	1.602; 1.607
1.595	34/3	1.593
1.577	23/4; 52/9; 29/5	1.583; 1.580; 1.577
1.563	6; 25/4	1.553; 1.559
1.539	?	—
1.530	56/9	1.526
1.523	44/7; 31/5	1.519; 1.523
1.512	38/3	1.513

B. Measurement of the 11/ Diffractions on the Corresponding Streaks in Fig. 12.

moreover, were for the most part capable of representation with good quantitative agreement, as will be seen from Table II A and B, either as diffractions with integral indices or as diffractions with fractional l index, the latter spots having in general intensities not very much less than, and in some cases about the same as, those of the normal integral index diffractions in these photographs. No diffraction spots were obtained with radial distances less than that of the 100 diffraction in these patterns.

Although solutions of various concentrations of cadmium iodide were used, and a considerable number of crystals of macroscopic size were present in most of the specimens crystallised from solution, no clear Laue-zone spot intensification nor any sign of Kikuchi lines was detected in any of the single-crystal transmission patterns. On the other hand, some large and well-formed crystals in the form of colourless hexagonal flakes about 2 to 3 mm. in diameter, were grown by evaporation of an aqueous solution of cadmium iodide at room temperature and, although it was diffi-

cult to detach chosen crystals from the matrix without deforming them, one such specimen was successfully mounted and yielded the pattern, Fig. 12, when the electron beam grazed its glassy smooth surface, *i.e.* the (001) plane. This Kikuchi line pattern was analysed by the method previously described,⁸ and was found to be in complete agreement with the structure proposed by Hassel. The electron beam was in this case nearly parallel to the [120] lattice row which meets the plate where the median of the strong central 211.0 band, lying along the axis of symmetry of the pattern, meets the shadow edge at right angles. If this [120] intersection be taken

as origin and two axes of co-ordinates be taken, positive x to the left along the shadow edge and z upwards along the $2\bar{1}\bar{1}\cdot 0$ band median, the equation to the Kikuchi line pair from any net plane (hkl) is

$$lz \cdot c/a = -hx + \left[\frac{h + 2k}{\sqrt{3}} \cdot L \pm \frac{\lambda L}{2a} \left(\frac{a}{d} \right)^2 \right],$$

where L is the camera length, λ the electron wave-length, and d is the (hkl) net-plane spacing. It will be seen from Fig. 12 that the intensities of the $10l$ and $12l$ groups of diffraction lines where l is odd are of similar magnitude to those with l even, whilst in the $11l$ group of diffraction lines only those with l even are observed. The nature of the spot pattern near the $[120]$ zone axis intersection also testifies to the fact that the true axial ratio of the structure is that given by Arnfelt and Hassel.

(ii) Specimens Prepared by Vaporisation *in vacuo*.

All specimens of this type showed, as found by Kirchner, more or less pronounced orientation on the collodion substrate with the same axis of orientation $[001]$, as in those prepared from solution. The patterns consisted of rings or arcs, together with the strong elliptic bands, similar to those in Figs. 2, 3 and 4, which were also sometimes discontinuously patchy though no marked spot patterns were observed. All the diffractions recorded in Table I were clearly visible in these patterns also. The clearest and most brilliant patterns were obtained from specimens which had been built up to suitable thickness by a single uninterrupted condensation from the vapour given off by the molten cadmium iodide *in vacuo*, rather than by an intermittent condensation with admittance of air for inspection of the specimen.

In some patterns from polycrystalline specimens certain anomalous diffractions occasionally appeared, which were sporadic in the sense that they were not always obtained and must therefore have differed in their origin from those due to lattice limitation effects. These rings were rarely observed with specimens prepared by vaporisation, but were frequently met with in patterns from polycrystalline films prepared from solution; some lay well within the 100 diffraction as may faintly be seen, for example, in Fig. 2. Again, in Fig. 3, the region between the 110 and 120 rings appears banded in the reproduction, although on the original plate this banded appearance can be seen to be due to a series of closely spaced and exceedingly fine rings. These sporadic rings may either be due to the presence of some material other than anhydrous cadmium iodide, or may possibly indicate a change from an unstable structure to that normally assumed by the material. Quarrell¹¹ has observed changes of this type occurring in thin metal films. A glance suffices to show that these anomalous diffractions have nothing to do with grease.

5. The Axial Ratio of Cadmium Iodide.

A value of the axial ratio of the lattice can be calculated from the data of Table I independently of either voltage or camera length, the accuracy being virtually that of the measurement of the diffraction pattern. The measurements of the diameters of the relatively sharp, clear $11l$ arcs ($l > 2$) are most suitable for this purpose. These are given in Table II, together with the corresponding hkl indices and the c/a values follow from the relation

$$\frac{c}{a} = \left\{ l^2 \left/ \left[\frac{a^2}{d^2} - \frac{4}{3}(h^2 + k^2 + hk) \right] \right. \right\}^{\frac{1}{2}},$$

¹¹ A. G. Quarrell, *Proc. Physic. Soc.*, 1937, 49, 279.

using the X-ray value $a = 4.240$ A. to which the (hko) spacings were referred for comparison. The mean value of c/a calculated from these

TABLE III.—AXIAL RATIO OF CADMIUM IODIDE.

Indices.	Data from Fig. 4.		Another Pattern Like Fig. 4.	
	d in A.	c/a .	d in A.	c/a .
114	1.800	3.214	1.803	3.228
116	1.551 ₅	3.220	1.551	3.218
118	1.331	3.226	1.331 ₅	3.228
11.10	1.152	3.234	1.148	3.224
11.12	1.003	3.224	1.007	3.238
	Mean $c/a = 3.224$.		Mean $c/a = 3.227$.	
	Mean $c/a = 3.226$.			

this ratio suggests that, as in the case of molybdenite, the c value of cadmium iodide is independent of crystal thickness.

6. Discussion.

1. In each case the positions of the diffraction arcs in Fig. 4 and the Kikuchi lines in Fig. 12 lead to the unit cell dimensions found by Arnfelt and Hassel. The relative intensities of the diffractions are also in good agreement with those required by the atomic co-ordinates deduced by Hassel. Thus the diffractions with l odd, which would correspond to half orders if Bozorth's unit cell were taken, only occur in the zones $10l$, $20l$, $12l$, $13l$, etc., for which $(h + 2k) \neq 3p$, and some have intensities about equal to those of diffractions with l even. No absolute comparison of observed and calculated electron diffraction intensities can be made either in the transmission patterns from thin films or in the reflection Kikuchi line patterns, owing to the considerable secondary scattering ("dynamic interaction") which occurs³ as a result of the high efficiency of scattering of electrons by the atoms. Nevertheless, apart from the factor representing the number of co-operating planes and that expressing the continuous intensity decrease as the indices of the diffractions increase, the intensities normally show the distribution required by the structure factor, excepting certain readily recognisable cases of diffraction spots whose intensities can be augmented by secondary scattering from an intense primary diffracted beam, or in the case of higher orders of Kikuchi lines which can receive secondary scattering from strong lower-order lines from the same plane. The structure factor calculated from the atom co-ordinates given by Hassel is

$$S^2 = A^2 + B^2,$$

where

$$A = \overline{Cd} \left[1 + \cos 2\pi \left(\frac{h+2k}{3} \right) \cdot \cos \pi l \right] + \overline{l} \left[\cos 2\pi \left(\frac{h+2k}{3} \right) \left\{ 2 \cos \frac{\pi l}{4} + \cos \frac{5\pi l}{4} \right\} + \sin 2\pi \left(\frac{h+2k}{3} \right) \left\{ \sin \frac{3\pi l}{8} - 2 \sin \frac{\pi l}{8} \right\} + \cos \frac{5\pi l}{4} \right]$$

and

$$B = \overline{\text{Cd}} \left[\sin 2\pi \left(\frac{h+2k}{3} \right) \cdot \cos \pi l \right] + \overline{\text{I}} \left[\cos 2\pi \left(\frac{h+2k}{3} \right) \cdot \sin \frac{3\pi l}{4} - \sin 2\pi \left(\frac{h+2k}{3} \right) \cdot \cos \frac{3\pi l}{4} - \sin \frac{3\pi l}{4} \right],$$

where $\overline{\text{Cd}}$ and $\overline{\text{I}}$ are the scattering powers of the cadmium and iodine atoms.

Since the atomic numbers of cadmium and iodine are 48 and 53 respectively, a simple approximate evaluation of sufficient accuracy for present purposes can be made by putting $\overline{\text{Cd}} = \overline{\text{I}}$, whence we have the values of S^2 given in Table IV.

TABLE IV.

$S^2/\overline{\text{Cd}}^2$ for $\text{Cd} = \overline{\text{I}}$ and :—			
l	$(h+2k) = 3p$ (e.g. 111, 301, etc.).	$(h+2k) = 3p+1$ (e.g. 101, 131, etc.).	$(h+2k) = 3p+2$ (e.g. 121, 201, etc.).
0, 8, 16	36	0	0
1, 9, 17	0	1.76	1.75
2, 10, 18	4	10.00	10.01
3, 11, 19	0	10.24	10.26
4, 12, 20	4	4	4
5, 13, 21	0	10.26	10.24
6, 14, 22	4	10.01	10.00
7, 15, 23	0	1.75	1.76

It may be noted that in the spot pattern of Fig. 9 the hko diffractions with $(h+2k) = 3p$ are very much stronger than the others, and although in this case multiple scattering will lead to a general evening-out of the intensities, the disparity between the corresponding structure factors $(2\overline{\text{Cd}} + 4\overline{\text{I}})^2$ and $(\overline{\text{Cd}} - \overline{\text{I}})^2$ is about 3600:1, and thus so large that the two groups of spots must still remain widely different in relative intensity.

2. A principal aim of the present investigation was to find whether very thin cadmium iodide crystals yield "fractional order" diffractions as a result of lattice limitation in the l direction. Kirchner,⁷ who first observed the elliptic banded effects with the orientated polycrystalline specimens, suggested that these bands must be due to very thin flakes acting practically like pure cross-gratings. Burgers¹² has given a striking illustration of the formation of such elliptic bands by means of photographs obtained with his reciprocal lattice demonstration apparatus, assuming various degrees of elongation of the points of the lattice, both with and without small imperfections of orientation of the crystal particles; following Kirchner, he also concluded that the circular arcs are due to relatively thick crystals, while the elliptic bands are produced by the very thin crystals. Kirchner's explanation and Burger's reciprocal lattice model demonstration of the effect fail, however, to take account of the intermediate stage between the three-dimensional and truly two-dimensional conditions which we have shown

¹² W. G. Burgers and J. J. A. Ploos van Amstel, *Z. Krist.*, 1936, **95**, 54.

to occur both in this case and previously with graphite, molybdenite and mica, in that with the thinnest crystals available the "rotation" streaks show abrupt increases in intensity in positions corresponding to normal and "extra" diffractions. For example, in Burger's model the rods are either wholly white, *i.e.* totally reflecting and thus correspond to a two-dimensional effect, or they consist of alternating wholly white and totally absorbing black sections, and thus represent three-dimensional conditions, the relative lengths of black and white sections being a function of the resolution of the lattice in the direction of lattice limitation. To illustrate the intermediate stage where streaks intensified by diffraction spots are formed, Burgers' reciprocal lattice rods should consist of wholly white sections alternating with darker (but not black) sections of appropriate lesser reflecting power. Thus, in agreement with Kirchner and Burgers, we consider that exceptional crystal thinness must clearly be the origin of the elliptic bands, since (i) we have observed the same effects from specimens prepared by evaporation of the solution, so that the bands can hardly arise from lattice disturbance due to partial decomposition of the cadmium iodide; (ii) we have already shown with graphite, molybdenite and mica flakes of exceptional thinness, but still several molecular layers in thickness, that the large amount of tolerance in the diffraction conditions necessary for such band formation is, in fact, realised. On the other hand, since true two-dimensional conditions, such as would practically obtain with crystals of a single molecular layer thickness, have so far not been realised, it is clear that Kirchner's and Burgers' postulate of thick crystals as giving rise to the sharp arcs superimposed on the banded regions is unnecessary. For example, our experiments with graphite and molybdenite, where virtually only the decrease in crystal size perpendicular to the layer planes affects the diffraction pattern, have shown that as crystal thickness is decreased and pure two-dimensional crystal form approached, bent or rotated single crystals yield diffractions corresponding to fractional as well as integral l indices, and not merely continuous linear elongation of spots of normal three-dimensional origin. In the case of the ring and arc patterns so far obtained from polycrystalline cadmium iodide, we have observed no definite fractional order diffractions sufficiently resolved for their accurate measurement and identification; nevertheless, it is apparent that the pattern is not the result of a simple superposition of normal arcs from thick crystals on uniform bands due to thin crystals, but is produced wholly by thin crystals, as is indicated by an important feature of the pattern. Thus, while there are sharp normal diffraction arcs lying on the faint elliptical bands whose (hk) indices are such that $(h + 2k) = 3p$ where $p = 0, 1, 2, 3$, etc., the others which have $(h + 2k) \neq 3p$ are very much less sharp, and the corresponding bands are relatively strong. The effect is most clearly seen in the $10l$ and $11l$ elliptic band series, and is particularly striking in Fig. 4.

More specific proof of the occurrence of "extra" diffractions was found in the fact that patterns like Fig. 11 were obtained, showing groups of spots on diffraction lines similar in nature to those obtained from the thinnest bent crystals of the three layer-lattice materials previously studied by us. It was found possible to assign fractional order l indices (with denominators < 9) to practically all the diffraction points lying along the diffraction lines, with a similar order of agreement to that obtained in the case of molybdenite, although these spots from

cadmium iodide were very fine and many of them rather faint. It is, of course, possible to obtain from the thinnest crystals sharp diffraction spots of considerable intensity in any position. Such spots have indefinite l indices, being analogous to a true two-dimensional effect, and cannot, of course, occur on rings or lines; they are due to the equivalent of an arbitrary arrest of rotation of very thin crystals. In the present case, the bending of the crystals was evidently produced by surface tension forces during evaporation of the solution. The total angle of curvature θ of each flake across the beam-width, B , can be calculated readily from the lengths of the streaks or spot rows such as occur in Fig. 11, whence the radius of curvature ρ is given approximately by B/θ . If we assume the middle layer of the crystal flake to be a neutral plane, the lattice constant a in this plane must be increased at the surface layers to $a + \delta a$ where $\frac{\delta a}{a} = \frac{t\theta}{2B}$, t being the total film thickness. Hence, if the layer planes remain at the same distance apart, the total range of variation of the effective axial ratio (c/a) will also be $t\theta/2B$. Taking $B = 0.01$ cm. and $t = 100$ Å. this would allow θ to be about 300° (thus $\rho = 0.002$ cm.) before the change in axial ratio near the surface would amount to $1^\circ/00$. If the above assumptions are justified, the definition and uniformity of axial ratio determinations from measurements of spot positions along the diffraction lines would appear, therefore, to be quite natural. It is possible, however, that such an ideal form of bending may not be realised, but that the bending might produce slipping of layers of the crystal over each other, or even a parallel flexure of the type suggested by Lotmar.¹³

3. In this and in the previous work on graphite and molybdenite it has been made clear that the "extra" diffractions to which fractional l indices have been assigned owe their origin to an anomalous diffracted intensity distribution which only comes into play when the crystal is exceptionally thin. So far no complete and quantitative treatment of the limited lattice interpretation of the "extra" diffraction phenomena in terms of intensity distribution has been undertaken. A preliminary examination of the dependence of position and intensity of the secondary maxima on the lattice limitation in the c direction of a layer lattice, as given by the Laue interference function for single scattering, shows that subsidiary maxima of considerable intensity are indeed to be expected in the vicinity of normal diffractions, but the agreement with observation is incomplete. We hope in the near future to carry out a more rigorous analysis.*

4. As previously in the case of graphite, molybdenite and mica, $00l$ diffractions from cadmium iodide are conspicuous by their absence. This is easy to understand, because in the case of crystals thin enough in the h and k directions for coherent transmission the crystal habitus is such that the lattice length in the l direction will be so short as to render the $00l$ diffractions virtually invisible through poor definition.

5. A rather curious feature of these experiments is the fact that, although many single crystals of cadmium iodide, ranging in thickness up to complete opacity to the beam, have been examined, in no case

¹³ W. Lotmar, *Z. Krist.*, 1935, **91**, 187.

* (Note added in Proof.) Since writing the above, we have carried out such an analysis and applied the results to the special cases of graphite and molybdenite.¹⁴

¹⁴ G. I. Finch and H. Wilman, *Ergeb. exakt. Naturwiss.*, 1937, **16**, 351.

were Kikuchi lines or similar secondary scattering effects ever observed ; on the other hand, such secondary effects are prominent in reflections from single crystals. In our experience this phenomenon is not confined to cadmium iodide, for we have made similar observations with a wide variety of crystals, including many organic crystals. On the other hand, it may be recalled that mica, graphite and molybdenite all give good Kikuchi line patterns by transmission ; possibly, with cadmium iodide and with other crystals of similar behaviour, it is a question of pronounced mosaicity in thin single crystal films, which disappears in the surface layers of the massive crystals obtained by crystallisation from solution.

7. Summary.

The diffraction of electrons by crystalline cadmium iodide has been studied.

In agreement with Hassel it has been found that the c -axial length is double that originally assigned by Bozorth. The electron diffraction and X-ray values of the axial ratio are in good agreement, whence it seems that c is independent of crystal thickness. Apart from the effect of certain disturbing factors of recognised origin, the electron-diffraction intensity distribution accords with the structure factor calculated from Hassel's atom co-ordinates.

Kirchner's explanation of the elliptic banded effects has been confirmed and extended in the light of the phenomena observed with very thin cadmium iodide and other layer-lattice crystals. Also, the alterations in Burger's reciprocal lattice model, necessary in order to take account of the new effects, have been indicated.

It has been recognised that in addition to extra diffractions of both spots and rings of fractional l -index value and attributed to lattice limitation effects, anomalous diffraction spots (but not rings) of indefinite l -index value may be produced by thin flakes exhibiting abrupt changes in curvature, such an effect being equivalent to an arbitrary arrest of rotation of a true cross-grating during recording of the pattern.

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A THEORY OF THE SURFACE TENSION OF ELECTROLYTES.

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It is a well-established fact that the surface tensions of aqueous and non-aqueous salt solutions are greater than that of pure water.^{1, 2} Thermodynamic considerations show that in these cases the solute is negatively adsorbed at the surface, and from the application of the Gibbs equation it is found that the surface excess corresponds to a layer of pure water of the order of one molecule thick. Heydweiller³ attempted to explain this negative adsorption of the solute in terms of the electrostatic attraction between the ions, and later Wagner⁴ was able to calculate by a rather complicated method the negative adsorption and the surface tensions of dilute solutions from considerations of the mirror image forces at the phase interface. This theory has been extended and simplified by Onsager and Samaras,⁵ who deduced the relation

$$\gamma = \gamma_0 + \text{const} \times c \log \frac{\text{const}}{c}$$

as the limiting law for the surface tension of dilute solutions. The problem has also been considered by Oka,⁶ by Ariyama¹⁶ and by Ssementschenko.¹⁷

The Effect of Ions on Surface Films.

The effect of ions on dissolved non-electrolyte molecules is to produce a change in their concentration in the vicinity of an ion; the effect of these ions on the solvent at the surface of the solution is to produce a reduction in the number of non-electrolyte molecules there, and so to produce a change in the surface tension. This change in the surface adsorption may be calculated in the following manner, which is based on the treatment suggested by the writer for the salting out of non-electrolytes in the bulk of the solution.⁷

Consider an element of surface ds ; let us find the effect on the non-electrolyte molecules contained in it of a hemispherical shell of thickness dr at a distance r from it, and containing n' ions per unit volume. The work done in moving an ion of charge $Z_i e$ from infinity up to a distance r from ds is

$$\int_{\infty}^r \frac{2\mu Z_i e}{D_0 r^3} dr = \frac{\mu Z_i e}{D_0 r^2} \quad \dots \quad (1)$$

¹ *International Critical Tables*.

² Kosakewitsch, *Z. physik. Chem.*, 1928, **133**, 5.

³ Heydweiller, *Ann. Physik*, 1910, (4), **33**, 145.

⁴ Wagner, *Physik. Z.*, 1924, **25**, 474.

⁵ Onsager and Samaras, *J. Chem. Physics*, 1934, **2**, 528.

⁶ Oka, *Proc. Phys.-Math. Soc. Japan*, 1932, (3), **14**, 649.

⁷ Belton, *Trans. Faraday Soc.*, 1937, **33**, 653.

where μ is the moment of the non-electrolyte molecules in the surface and D_0 is the dielectric constant of the medium. There are $2\pi r^2 n' dr$ ions in the shell; the work done in building up the total ionic environment of ds is then

$$n' \int_{\infty}^b \frac{\mu \sum z_i \epsilon}{D_0 r^2} 2\pi r^2 dr = \frac{2\pi n' b \mu \sum z_i \epsilon}{D_0} \quad (2)$$

where b is the distance of nearest approach of an ion to the surface.

There will also be a contribution due to the change in polarisation of the non-electrolyte molecules in the presence of ions. The work done in moving an ion of charge $z_i \epsilon$ from infinity to a distance r from ds containing non-electrolyte molecules of polarisability α is

$$\int \frac{2\alpha z_i^2 \epsilon^2}{D_0^2 r^5} dr = \frac{\alpha z_i^2 \epsilon^2}{2D_0^2 r^4} \quad (3)$$

and the work done in forming the total ionic environment of ds is

$$n' \int_{\infty}^b \frac{\alpha \sum z_i^2 \epsilon^2}{2D_0^2 r^4} 2\pi r^2 dr = \frac{2\pi n' \alpha \sum z_i^2 \epsilon^2}{2D_0^2 b} \quad (4)$$

If n_0 is the number of non-electrolyte molecules per unit area in the surface when no salt is present, then Boltzmann's theorem gives for the number in the presence of salt in the element ds

$$nds = n_0 e^{-\frac{2\pi n' b \mu \sum z_i \epsilon}{D_0 kT} - \frac{2\pi n' \alpha \sum z_i^2 \epsilon^2}{2D_0^2 kT}} ds \quad (5)$$

Application to Aqueous Salt Solutions.

The values of n calculated from (5) may be compared with those found from the Gibbs equation according to which

$$\frac{d\gamma}{dm} = 2kT\Gamma \frac{m}{55.55} \left(\frac{1}{m} + \frac{d \log f_{\pm}}{dm} \right) \quad (6)$$

where γ is the surface tension of the solution, m the concentration of the salt, f_{\pm} its activity coefficient, and Γ the surface excess of water.

TABLE I.

m .	Γ .	$n(1)$.	$n(2)$.
0.5	1.26×10^{15}	1.37×10^{15}	1.30×10^{15}
1.0	1.18	1.32	1.25
2.0	0.95	1.22	1.15
3.0	0.75	1.13	1.06

Table I gives some values of Γ and n for various concentrations of uni-univalent electrolyte.

The third column gives $n(1)$ taking n_0 as 1.43×10^{15} (obtained from the molecular volume of water),

while the fourth gives $n(2)$ with n_0 taken as 1.35×10^{15} (obtained by assuming the value of n for a 0.1 M solution to be given by the Gibbs equation, and calculating n_0 from it by substitution in (5)). D_0 has been taken as the dielectric constant of water, and b as 4A, the order of the thickness of the water layer on salt solutions. The second term in the exponential in (5) is small and may be neglected in comparison with the first.

The values of n calculated from (5) are thus of the same order of magnitude as those calculated from the Gibbs equation, but the agreement becomes less satisfactory as the salt concentration increases.

The application of the theory to dilute salt solutions may be conveniently made by combining equations (5) and (6) to give

$$\frac{d\gamma}{dm} = n_0 e^{-2\pi n' b \mu \Sigma z_i e / D_0 k T} 2kT \frac{m}{55.55} \left(\frac{1}{m} + \frac{d \log f_{\pm}}{dm} \right) \quad (7)$$

and comparing the values so obtained with experimental results. Values of $d\gamma/dm$ calculated in this way are given in Table II. Here n_0 was taken as 1.35×10^{15} and b as 4 Å. as before; $d \log f_{\pm}/dm$ was calculated from the empirical equations of Harned.⁸ The surface tensions of dilute solutions are not very much different from that of water, and their accurate measurement presents some difficulty. The values of $d\gamma/dm$ in Table II have been calculated from the data of Schwenker;⁹ the third column gives $(\gamma - \gamma_0)/m$, and the fourth $(\gamma_2 - \gamma_1)/(m_2 - m_1)$. The lack of constancy of the values in the third column shows that the relation between surface tension and concentration is not linear, $\gamma = \gamma_0 + km$, which is found to hold for stronger solutions.

The measurements of Schwenker were made at 0° C., while the values calculated from (7) refer to 25°; these, however, will be little different from those measured at 25° as $d\gamma/dm$ changes only slightly with temperature—for example, for both

TABLE II.

Salt.	m .	$d\gamma/dm$ (calc.).	$(\gamma - \gamma_0)/m$.	$(\gamma_2 - \gamma_1)/(m_2 - m_1)$.
NaCl	0.015	1.92	2.23	—
	0.030	1.89	2.06	1.89
	0.050	1.87	1.96	1.82
	0.075	1.85	1.94	1.88
	0.100	1.83	1.93	1.92
	0.125	1.83	1.87	1.61
	0.150	1.81	1.84	1.72
	0.50	1.76	1.73	1.73
	1.00	1.78	1.73	1.73
KCl	0.015	1.92	2.23	—
	0.030	1.89	2.16	2.09
	0.050	1.86	2.07	2.06
	0.075	1.83	2.04	1.88
	0.100	1.81	1.94	1.81
	0.130	1.79	1.85	1.40
	0.160	1.78	1.67	—
	0.50	1.70	1.67	1.67
	1.00	1.66	1.67	1.67

sodium and potassium chlorides $\gamma - \gamma_0$ is the same for solutions up to 2 M for temperatures between 0° and 30° (*cf.* Inter. Crit. Tables). It should be noted that the surface tensions of very dilute salt solutions are less than that of water, indicating a positive adsorption of the solute.

Application to Non-Aqueous Solvents.

The increase in surface tension which occurs when an inorganic salt is dissolved in an organic solvent indicates that there is a surface excess of the solvent. The surface concentration may be calculated from (5) on using appropriate values of the dielectric constant and the distance of nearest approach. In most such cases for which surface tension data are available, the activity coefficient of the salt is not known, and so an approximate form of the Gibbs equation, with concentrations instead of activities, must be used to calculate the surface adsorption.

⁸ Harned, *J. Amer. Chem. Soc.*, 1920, 42, 1808; 1922, 44, 252.

⁹ Schwenker, *Ann. Physik*, 1931, 11, 525.

The surface tensions of solutions of sodium iodide at various concentrations in each of several different solvents have been measured by Kosakewitsch²; the surface concentration has been calculated from them in the following manner. For such a binary solution

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$

where the subscripts 1 and 2 refer to salt and solvent respectively, Γ to the surface concentration and μ to the chemical potential. When $\Gamma_1 = 0$

$$\begin{aligned} d\gamma &= -\Gamma_2 d\mu_2 \\ &= \Gamma_2 \frac{N}{100} 2kT d \log N \end{aligned}$$

where N is the concentration of the salt in moles per cent. Hence

$$\Gamma_2 = \frac{d\gamma}{dN} \cdot \frac{100}{2kT}$$

The values of Γ so calculated show very little variation with concentration; their smoothed values are given in the third column of Table III. The number (n_0) of solvent molecules per sq. cm. of surface

TABLE III.

Solvent.	D_0 .	Γ .	A.	n .	b .	l .	r .
C_2H_5OH	25.8	0.3×10^{15}	23	0.43×10^{15}	5.7	7.8	3.7
C_2H_7OH	22.2	0.2	23	0.43	10.4	10.1	4.7
$(CH_3)_2CO$	21.7	0.2	23	0.43	10.5	8.4	4.2
$i-C_4H_9OH$	15.9	0.03	46	0.22	19.5	12.4	24.6
C_4H_8OCHO	41.7	0.35	25	0.40	7	—	—

of the pure solvent has been calculated from the known areas of these molecules in surface films^{*}; that of furfural was assumed to be of the order of 25 \AA^2 . There is again some uncertainty in the value to be ascribed to b , the distance of nearest approach to the surface; instead, therefore, of calculating n for an assumed value of b from (5) and comparing with the surface excess obtained from the Gibbs equation, it seems preferable to calculate b from (5) assuming that n is equal to Γ , and to see whether a reasonable figure is obtained. The sixth column gives the values of b calculated in this way, and the seventh the length of the adsorbed molecules (which will be orientated vertically in the surface) from the known sizes of the atoms and the interatomic distances.[†] The b values appear to be of reasonable magnitude and are in the right order for the different solvents considered. The mean radii of the ions of sodium iodide in different solvents have been calculated from the Debye theory by Hartley and Bell¹⁰; their values are given in the last column and, although mostly lower than those given here, are in the same order. It should be pointed out, however, that complications may be introduced by the partial dissociation of the salt, and further that the theory does not explain the apparently small change in adsorption with salt concentration.

^{*} Cf. Adam, *The Physics and Chemistry of Surfaces*.

[†] Cf. Sidgwick, *The Covalent Link in Chemistry*.

¹⁰ Hartley and Bell, *Trans. Faraday Soc.*, 1927, 23, 396.

The Effect of Ion Size.

The surface adsorption for different solutes should depend on the value of b , that is on the nature of the ions and the extent of solvation. The surface concentrations of water at the surface of alkali chloride solutions differ with the dissolved salt; thus for 0.5 M solutions of lithium chloride, sodium chloride and potassium chloride the values calculated from the Gibbs equation are 18.2, 20.8, and 21.0 in moles per sq. cm. $\times 10^{10}$, and for 1 M solutions the corresponding figures¹¹ are 14.8, 19.5 and 20.5. The greater the value of b , the less is the exponential term in (5) and the less is the calculated n . Hence b is least for potassium and greatest for lithium, which is in agreement with the order of hydration found from transport experiments.

Comparing two such solutions we have

$$\Gamma_1 = n_0 e^{-Ab_1} : \Gamma_2 = n_0 e^{-Ab_2}$$

and hence

$$\frac{\log n_0 - \log \Gamma_1}{\log n_0 - \log \Gamma_2} = \frac{b_1}{b_2} \quad (11)$$

The relative values of b calculated in this way referred to $b_{K^+} = 1$ are given in Table IV; the last line gives the relative values from transport data.

TABLE IV.

Salt.	KCL.	NaCl.	LiCl.
0.5 M	1	1.09	2.23
1.0 M	1	1.35	3.31
—	1	1.55	2.6

For solutions of sodium, potassium and lithium iodides in methyl alcohol it is found that $d\gamma/dm$ and consequently Γ are in the order $K > Na > Li$ for solutions of 0.5 moles per cent., while for 2.0 moles per cent. the order is $Na > K > Li$.

Transport data in methyl alcohol show that the ion sizes for lithium and potassium are about the same and are greater than that for sodium.

Application to Ternary Solutions.

Measurements of the surface tensions of solutions containing both sodium and potassium chlorides¹² show that these salts act independently in their influence on the amount of water adsorbed at the surface. The adsorption increases with an increase in the relative amount of potassium chloride in solutions of the same total salt concentration. According to equation (5) the only difference in the salting out in the surface layer will be due to the difference in the values of b for the sodium and the potassium ion; the effect of replacing the former by the latter will be to reduce b and so to increase the number of adsorbed water molecules—which is in accord with the experimental result.

Solutions containing salts and hydrochloric acid show a similar behaviour. The effect of adding 0.1 M acid is to reduce the water adsorption by 1.4, 1.3 and by 1.6 moles per sq. cm. $\times 10^{10}$ for sodium, potassium and lithium chlorides, and by rather larger amounts for the alkaline earth chlorides in 0.5 M solutions.¹³ The addition of larger concentrations of hydrochloric acid to sodium chloride solutions produces the same effect. If solutions of the same total concentration are

¹¹ Belton, *Trans. Faraday Soc.*, 1937, 33, 440.

¹² *Ibid.*, 1935, 31, 1413.

¹³ *Ibid.*, 648; 1936, 32, 1717.

compared, there appears to be very little difference in the amount of water adsorbed, which, however decreases with the total ionic concentration. The size of the hydrogen ion is less than that of sodium, and so the replacement of the latter by the former in solutions of the same total ionic concentration should produce an increased adsorption; this is borne out by the experimental figures, which show a slight increase with increasing hydrochloric acid concentration. The behaviour of solutions containing only hydrochloric acid (and hydrobromic) are difficult to explain, for the surface tension decreases with increasing concentration, indicating positive adsorption of the acid.

It should also be possible to predict the changes in adsorption at the surface of aqueous solutions containing a non-electrolyte and a salt. Systems of this type¹⁴ show a diminution in the water adsorption with increasing salt concentration, but the non-electrolytes were present in too small amounts for any change to be shown in their adsorption. The influence of lithium chloride on the adsorption at the surface of aqueous ethyl alcohol solutions has been investigated by Butler and Lees,¹⁵ who found that an increase in the lithium chloride concentration reduced the surface adsorption of both water and alcohol, but the latter to a greater extent. For example, with 6.4 moles per cent. alcohol the water adsorption was reduced from 103 to 47, while that of alcohol fell from 42 to 41; and for 25 moles per cent. of alcohol the former fell from 53 to 21 and the latter from 57 to 52. According to equation (5) the ratio of the water adsorptions will be $\Gamma_1/\Gamma_2 = e^{x_2 - x_1}$ and of the alcohol adsorptions $\Gamma'_1/\Gamma'_2 = e^{x'_2 - x'_1}$ where x is the appropriate index. All other terms except μ will be equal, and hence as the moment of water is greater than that of alcohol $(x_2 - x_1) > (x'_2 - x'_1)$ and $\Gamma_1/\Gamma_2 > \Gamma'_1/\Gamma'_2$ which agrees with the experimental result although the magnitude of the difference is greater than expected from the difference in μ .

Summary.

The extent of the salting out of non-electrolyte molecules in films adsorbed at the surface of solutions of electrolytes is shown to be related to the polarisability and the permanent moment of the non-electrolyte, the charge on the ions and the dielectric constant of the medium. The adsorption of water at the surface of aqueous salt solutions calculated in this way is found to be in agreement with the values obtained from the Gibbs equation. The behaviour of electrolytes in non-aqueous solutions is shown to agree with the theory, on the basis of which the sizes of molecules in the surface have been calculated and values of a reasonable order of magnitude obtained. The effect of ion size is discussed, and the relative sizes of lithium, sodium and potassium ions in aqueous solution are calculated from adsorption data, and are found to agree with those obtained from transport measurements. The theory is also in qualitative agreement with the behaviour of ternary solutions.

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¹⁴ Belton, *Trans. Faraday Soc.*, 1935, **31**, 1420.

¹⁵ Butler and Lees, *J. Chem. Soc.*, 1932, 2097.

¹⁶ Ariyama, *Bull. Chem. Soc. Japan*, 1936, **11**, 687; 1937, **12**, 32, 38.

¹⁷ Ssementschenko, *Koll. Z.*, 1932, **60**, 177; 1935, **73**, 24, 30.

THE p_H OF DISTILLED WATER, AND THE MEASUREMENT OF THE HYDROLYSIS OF AMMONIUM SULPHATE, NITRATE, CHLORIDE, AND ACETATE.

By J. A. CRANSTON AND H. F. BROWN.

Received 7th July, 1937.

The direct determination of the degree of hydrolysis of salts such as ammonium chloride is attended with certain difficulties owing to the absence of buffer action, and because their reaction in aqueous solution is within two p_H units of neutrality. For these reasons specially pure water must be used in preparing solutions of these salts; in particular, the exclusion of carbon dioxide is essential. Water prepared in a Bousfield still,¹ when ordinary precautions are taken to exclude carbon dioxide, has a reaction of about 5.7, and a specific conductivity of about 10^{-6} r.o. Assuming that the excess conductivity over that of pure water is due to carbon dioxide, the calculated p_H value is 5.7, in agreement with the experimental one.

Purification of Water.—The starting-point was freshly prepared water obtained from the still and having a reaction measured by the glass electrode of 5.7. Air from out of doors was purified by passing it in succession through solutions of potassium hydroxide and dilute sulphuric acid, three large soda lime towers, concentrated sulphuric acid solution, and finally through conductivity water. The passage of this air through the water increased its reaction to 7 in one hour and to about 8.0 in four hours, at which value it remained constant during the passage of air for eight hours. This experiment was repeated several times, and the final reaction of the water was always between 7.9 and 8.1. The air of the laboratory is normally free from acid fumes but exposure of the water to it for a few seconds altered the reaction to less than 7.0. Further passage of pure air restored it to about 8.0 even after it had remained in the electrode chamber for some days. There is little doubt that carbon dioxide from the atmosphere is responsible for this rapid change, and the absence of progressive alkalinity on standing shows that alkali from the glass electrode is not dissolved in appreciable amount.

The final value of 8.0 is in agreement with that obtained by Beans and Oakes² who concluded that the p_H of pure water was 7.9. These workers were the first to measure the p_H of water directly by the use of an electrode. It may be remarked that there is no *a priori* reason why the ionic product of pure water should not be less than that of water containing an electrolyte.³ Kolthoff and Kameda⁴ give the p_H of pure water as 7, but their measurement was done by an indicator, and therefore in presence of electrolytes.

Later work,⁵ however, has shown that the value 7.9 is probably due to the presence of ammonia, the last traces of which are not removed from

¹ Bousfield, *J.C.S.*, 1912, 1443.

² Beans and Oakes, *J.A.C.S.*, 1920, 42, 2116.

³ Brönsted, *ibid.*, 761.

⁴ Kolthoff and Kameda, *ibid.*, 1931, 821, 825.

⁵ Ellis and Kiehl, *ibid.*, 1935, 2139, and 2144.

solution by the passage of pure air. Ellis and Kiehl have distilled conductivity water in a current of pure air from a variety of reagents and found that distillation from phosphoric acid best retains the ammonia and consistently yields water with a reaction of 7.0. This is somewhat surprising as it is known⁶ that the passage of a gas through a solution of an ammonium salt always yields some ammonia. Beans and Oakes in their previous work had used phosphoric acid and obtained inconsistent results. We have repeated this work. Phosphoric acid, previously heated to drive off volatile impurities, was added to conductivity water from the still, and the solution distilled in an all Pyrex apparatus. A current of purified air was passed through the receiving flask, and through the empty electrode chamber. The distillate was then siphoned into the electrode chamber with pure air bubbling through continuously. In ten distillations, seven gave water with a reaction between 6.9 and 7.1 and three between 6.7 and 7.3.

Experimental.

The glass electrode is free from most of the limitations which prevent the use of the hydrogen or quinhydrone electrodes with many electrolytes. Neither of the last two can be used to measure the p_H of solutions of ammonium salts with accuracy. As the authors have recorded elsewhere,⁷ the glass electrode is particularly suitable for the measurement of unbuffered solutions like those of a pure salt or of water itself.

A detailed description of the apparatus, the method of preparation of the glass electrodes, the method of their calibration directly against the hydrogen electrode, and the experiments done to test the effect of neutral salts on the glass electrode have been published elsewhere.^{7, 8} The recording instrument is a McFarlane-Pye compensated valve potentiometer.⁹ In the present work, the lid of the electrode chamber carried two seasoned glass electrodes, a bridge containing agar-potassium chloride, a stirrer with a mercury seal, an L-shaped inlet tube for air, the bottom of the L almost touching the bottom of the electrode chamber and bearing some half a dozen tiny holes, an air outlet passing to a soda lime tube, and a small rubber stopper in the position later to be occupied by a burette. All these accessories were fitted tightly into the lid by means of rubber stoppers and the whole inner surface was then coated with pure paraffin wax. To minimise possible contamination from the agar bridge, it was kept above the surface of the water except during readings. The salt solution to be added to the electrode chamber was prepared in a 50 c.c. burette to the top of which a glass tube containing a ground glass stopper and side tube was sealed. Air, purified as already described, was passed through 200 c.c. of conductivity water contained in the electrode chamber and through 40 c.c. of water contained in the burette until the reaction reached about 7. A weighed amount of the salt, purified by a method* previously described,¹⁰ and contained in a weighing bottle narrow enough to fit inside the top portion of the burette, was emptied into the burette. A solution of known concentration was thus obtained, and portions of it were run into the electrode chamber to give solutions of the required concentrations. In this way, carbon dioxide-free water was prepared, and solutions of ammonium chloride, ammonium nitrate, ammonium sulphate, and ammonium acetate made up of various concentrations ranging from N/10 to N/2100 and their reaction measured, all without coming into contact with atmospheric carbon dioxide. The temperature for all experiments was maintained at 15° C.

⁶ Denham, *J.C.S.*, 1908, 41.

⁷ Cranston and Brown, *J. Roy. Tech. Coll.*, 1937, 4, 46.

⁸ *Ibid.*, 32.

⁹ *J. Sci. Instruments*, 1933, 10.

* Except that ammonium acetate was recrystallised from methyl alcohol.

¹⁰ Cranston and Brown, *J. Roy. Tech. Coll.*, 1937, 4, 54.

The experimental results obtained for ammonium chloride are shown in Table I. The third column gives the calculated hydrogen ion concentration, and the fourth the value of the hydrolysis constant calculated as $[H^+]^2/v$. The results for the other three salts gave equally smooth curves when the p_H was plotted against v ; so, for convenience of comparison, interpolated values at selected dilutions are shown together in Table II. The mean value of the hydrolysis constant for ammonium chloride was found from Table I to be 1.4×10^{-10} , which may be compared with the indirect value of 2.5×10^{-10} , calculated from the ionic product of water and the dissociation constant of ammonium hydroxide. The only other direct determinations of this constant that appear to have

TABLE I.—AMMONIUM CHLORIDE.

v , Litres per Gm.- equivalent.	p_H .	$[H^+] \times 10^7$.	$[H^+]^2/v \times 10^{10}$.
∞	7.0	—	—
1078	6.52	3.02	0.96
595	6.36	4.36	1.14
321	6.18	6.61	1.40
128	5.98	10.5	1.40
62.6	5.80	15.8	1.58
31.8	5.66	21.9	1.53
22.65	5.59	25.7	1.50
13.21	5.49	32.4	1.39
			Mean 1.4

been done are those by Hill¹¹ and by Job.¹² Hill estimated the amount of ammonia formed by hydrolysis by passing air through a solution of an ammonium salt of known concentration "at nearly 100° C.," collecting in distilled water the ammonia evolved, and calculating its amount by the

TABLE II.— p_H VALUES AT VARIOUS DILUTIONS.

v , Litres per Gm.- equivalent.	NH_4NO_3 .	NH_4Cl .	$\frac{1}{2}(NH_4)_2SO_4$.	$CH_3 \cdot COO \cdot NH_4$.
10	5.43	5.42	5.63	7.16
20	5.56	5.56	5.75	7.15
50	5.74	5.75	5.88	7.14
100	5.89	5.92	6.01	7.11
200	6.04	6.07	6.14	7.08
400	6.22	6.24	6.32	7.07
600	6.33	6.36	6.37	7.05
1000	6.45	6.51	6.55	7.04
∞	7.05	7.0	7.16	7.12

increase in the conductivity of the water. The mean value of the hydrolysis constant for the three concentrations used ($v = 1, 5$, and 25) was 6.7×10^{-8} for ammonium chloride and 6.2×10^{-8} for ammonium nitrate. The method of bubbling air through an ammonium salt may

be criticised on the grounds that progressive hydrolysis would be induced, and also that a volatile acid would be evolved along with the ammonia. Job discussed a method whereby the dissociation constant of ammonium hydroxide could be obtained by measuring the hydrogen ion concentration of solutions of ammonium salts during titration with hydrochloric acid. The hydrolysis constants of ammonium salts could then be calculated, and he obtained the value of 3.2×10^{-10} at 16° C. for "various ammonium salts" without specifying the salts and without giving any experimental details.

Discussion of Results.

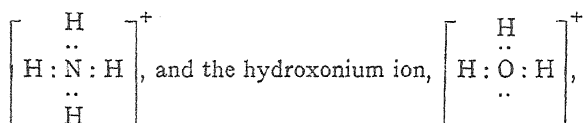
It is noted that the p_H values for ammonium chloride and for ammonium nitrate in Table II are identical within the experimental error. The values for ammonium sulphate are consistently higher,

¹¹ Hill, *J.C.S.*, 1906, 1273.¹² Job, *C.R.*, 1924, 1317.

especially for the more concentrated solutions, than those for the chloride and the nitrate. This may be accounted for by the smaller degree of dissociation of this uni-bivalent salt at corresponding dilutions of the two uni-univalent salts.

The reaction of ammonium acetate, as expected, is scarcely affected by dilution.

Some theoretical interest arises from this work. The question of the strength of the ammonium radical has been discussed in a series of articles,¹³ and the view expressed that ammonium hydroxide may be regarded as an intrinsically strong base in spite of the basic weakness of solutions of ammonia, because the ammonium ion is unstable in presence of hydroxyl ions. Thus what is usually represented as undissociated ammonium hydroxide may be NH_3 and H_2O . If this view is correct, the instability of the ammonium ion should be shown in solutions of ammonium salts by an enhanced value of the hydrogen electrode potential; for, if the ion can yield a proton to a hydroxyl ion, it should have some tendency to yield it to an electrode. A comparison of the electronic formulæ of the ammonium ion,



shows that if the latter can affect an electrode, the possibility that the former may also do so must not be ignored.

This work shows, however, that the potentials obtained with ammonium salts are just those expected on the hypothesis that ammonium hydroxide exists as a weak base; and no evidence is obtained of the assumed instability of the ammonium ion.

Summary.

1. The measurement of the p_H of pure water is discussed, and some experiments described.
2. The effect of dilution on the p_H value of solutions of ammonium chloride, ammonium nitrate, ammonium sulphate, and ammonium acetate has been measured.
3. The hydrolysis constant for the first two of these salts has been calculated to be 1.4×10^{-10} at $15^\circ C$.

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¹³ *Chem. and Ind.*, 1923, 164, 343, 448, 564, 578, 641, and 744.

ADSORPTION AND THE WETTABILITY OF SOLID SURFACES.

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The Equation of Dupré.

The conditions for equilibrium at the line of contact where the liquid-vapour interface of a pure substance meets the plane surface of a solid are given by the equation of Young and Dupré,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad . \quad . \quad . \quad (1)$$

where θ is the angle of contact (wetting angle), and γ_{SV} , γ_{SL} and γ_{LV} stand for the surface free energies of unit areas of the solid-vapour, solid-liquid, and liquid-vapour interfaces respectively. The term γ_{SV} is to be distinguished from the surface energy which the uncontaminated solid would have *in vacuo*, which we shall represent by the symbol γ_{SO} .

If W is the work necessary to pull apart the liquid and solid phases and produce, instead of 1 cm.² of solid-liquid interface, 1 cm.² each of solid-vapour and liquid vapour interfaces, we have

$$W = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad . \quad . \quad . \quad (2)$$

or, eliminating $(\gamma_{SV} - \gamma_{SL})$ between (2) and (1),

$$W = \gamma_{LV}(1 + \cos \theta) \quad . \quad . \quad . \quad (3)$$

in which the terms on the right-hand side are measurable in favourable cases.

It is to be noted that W is *not* the "work of adhesion" as ordinarily understood, though it is the work of adhesion as generally *defined*.¹ This is because the free surfaces produced by pulling the joint asunder are not those of the pure solid and pure liquid, but the former, in particular, will be contaminated with a fully-developed adsorbed film in equilibrium with the saturated vapour of the liquid. The solid, especially if soluble and capillary active, will also diminish the energy of the free liquid surface.² With many solids, such as charcoal, silica, and the like, this second effect is not serious; but that of the vapours of the liquids on the solid surfaces may run into hundreds of dynes.

¹ The work of adhesion as usually understood, and as specifically stated by Harkins, is $(\gamma_{SO} + \gamma_{LO} - \gamma_{SL})$ where γ_{LO} is the surface tension of the pure liquid; Harkins, Brown and Davies, *J. Amer. Chem. Soc.*, 1917, 39, 354; Harkins and Cheng, *ibid.*, 1921, 43, 35. Most authors, however, including Adam (*The Physics and Chemistry of Surfaces*, p. 10) and Bartell (*Z. physik. Chem.*, 1927, 130, 715) define it as the work required to separate the liquid and solid phases, a definition which has led to its incorrect use (instead of W) in equation (3) above.

² We are indebted to N. K. Adam (*private communication*) for pointing this out.

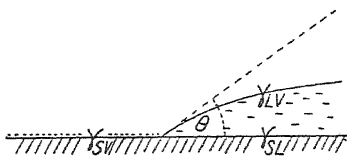


FIG. 1.

The work W clearly affords no true measure of the forces which bind to the solid the layer or layers of liquid immediately adjacent to it. There will, on the other hand, be a close connection between W (or θ) and the nature and properties of the adsorbed phase. If, for example, a liquid were found capable of *spreading*³ on a solid in the presence of its own saturated vapour (i.e. if $\theta = 0$, $W = 2\gamma_{LV}$), we should have evidence that the molecules forming the adsorbed film at saturation, even if differently aggregated from those in the bulk liquid, were at least capable of passage into the latter state without discontinuity. Such a system could under no circumstances give rise to supersaturation phenomena in the vapour phase, for, as Freundlich⁴ has pointed out, if a liquid wets a solid completely, the adsorption isotherms of its vapour should become asymptotic to the adsorption axis at *saturation*. Conversely, if there is a finite contact angle, we can be sure that the aggregational states in the adsorbed phase and in the bulk liquid must differ in some way or other.

This interrelation between the wettability of surfaces and the nature and properties of the adsorbed phase formed from the vapour has been rather overlooked; thus, whilst Hardy⁵ states that in general *pure* liquids appear incapable of spreading on clean plane surfaces of solids in the presence of their saturated vapours, the supposed formation of adsorbed films having properties identical with the bulk liquids forms the basis of more than one current theory of adsorption.

A detailed study of the adsorptive properties and wettability of cleavage surfaces of mica (muscovite) has provided much evidence in favour of Hardy's viewpoint. To give only one instance, a drop of methyl alcohol spreads rapidly when placed on freshly-split mica when the experiment is done in air, but in the presence of its own saturated vapour it will not do so; if the spread film formed in air is brought under a jet of the supersaturated vapour of the alcohol, it immediately gathers back again into lenses.⁶

Physically and Chemically Adsorbed Films.

Where the adsorbed film formed by the vapour can be pictured as a Langmuir monolayer in which the molecules have fixed points of attachment (chemisorption), no difficulty arises over the conception of a surface phase separated from the solid-liquid interface by a line of discontinuity. It is, however, certain that such discontinuity (finite contact angle) can occur in the most typical cases of physical adsorption, even, for example, when the adsorbed film is so thick as to give rise to interference colours.⁶

Gibbs⁷ remarked that the surface energy of a solid, which is the work required to form 1 cm.² of new surface, will, in general, differ from the surface *tension* which measures the work necessary to produce unit increase in the area of a large already existing surface by a process of stretching which brings no additional atoms into the interface. It has been pointed out⁸ that a film containing only *chemi* sorbed molecules between

³ By spreading is meant the spontaneous indefinite extension, or disappearance of the edges, of a drop placed on a large surface (the secondary spreading of Hardy).

⁴ Freundlich, *Kapillarchemie*, 1922, 220.

⁵ Hardy, *Proc. Roy. Soc., A*, 1913, 88, 313; *Phil. Mag.*, 1919, 38, 49

⁶ Bangham, Mosallam and Saweris, *Nature*, 1937, 140, 237.

⁷ *Collected Works*, 1928, 1, 315

⁸ Bangham, *Trans. Faraday Soc.*, 1937, 33, 805.

which no tangentially directed repulsive forces are acting could under no circumstances influence the surface tension of the underlying solid, though it would reduce the surface energy. The only force opposing the spreading of a drop of the liquid would therefore be its own surface tension. With films that are *physically* adsorbed, on the other hand (the molecules having no fixed points of attachment), the effects on the surface tension and surface energy become equal, and identifiable as a surface *pressure* which would oppose spreading. Where a liquid shows inclination to spread on an uncontaminated surface, but gathers back into lenses when the vapour phase becomes saturated, we may be sure that physical adsorption is playing an important part, though the possibility of an underlying layer of chemisorbed molecules would not be precluded. It is, indeed, difficult to imagine a mechanism whereby the short-ranged forces operative in chemisorption could give rise to any spreading effects at all.

Immersional Wetting; The Changes of Free and Total Energy.

There being no means available for measuring the surface energies of solids, it is convenient to subtract the surface energy γ_{SO} of the pure solid from both sides of equation (1), obtaining, with a change of sign,

$$\begin{aligned} (\gamma_{SO} - \gamma_{SL}) &= (\gamma_{SO} - \gamma_{SV}) + \gamma_{LV} \cos \theta \\ F_L &= F_V + \gamma_{LV} \cos \theta \end{aligned} \quad (4)$$

where F_L is written for the surface energy *lowering* produced by immersion in the liquid, and F_V for that produced by exposure to the saturated vapour. It has been emphasised that the wetting angle θ is determined, not by F_L but by $(F_L - F_V)$.

In equation (4) the terms on the right-hand side are capable of experimental determination, though conditions render such measurements difficult, and in no case, as far as we know, are full data available. For the evaluation of F_V it is necessary to know the adsorption per cm.², which we write Γ , as a function of the pressure p , *i.e.* the adsorption isotherm; we have then,⁸ writing Gibb's adsorption equation in integrated form

$$\begin{aligned} F_V &= RT \int_{p=0}^{p=p_0} \Gamma d \log_e p, \\ F_L &= RT \int_{p=0}^{p=p_0} \Gamma d \log_e p + \gamma_{LV} \cos \theta \end{aligned} \quad (5)$$

where p_0 is the saturation pressure of the normal liquid at the experimental temperature T . Some tentative values of F_V for charcoal exposed to the saturated vapours of common liquids are given in the paper which follows.⁹

The heat of wetting ($-\Delta H$), or diminution of heat content which accompanies immersion in the liquid is given by the Gibbs-Helmholtz equation¹⁰

$$-\Delta H = F_L - T \frac{dF_L}{dT} \quad (6)$$

⁹ Bangham and Razouk, *Trans. Faraday Soc.*, 1937, **33**, 1463.

¹⁰ Not by $F_V - T \frac{dF_V}{dT}$ as stated by Williams, *Proc. Roy. Soc. Edin.*, 1918, **38**, 23, and others.

Combining this equation with (4) we have

$$-\Delta H = \left(F_v - T \frac{dF_v}{dT} \right) + \left(\gamma_{LV} \cos \theta - T \frac{d\gamma_{LV} \cos \theta}{dT} \right) \quad (7)$$

The expression within the first bracket represents the heat evolved by the formation *from the liquid* of an adsorbed film in equilibrium with the saturated vapour; it is less than the total heat of adsorption by an amount equal to the normal heat of condensation of just sufficient vapour to form the film. The expression within the second bracket represents heat generated when the surface, already saturated, is plunged into the liquid; in the special case where $\theta = 0$, this would reduce to the total surface energy of the normal liquid. It is to be noted that in equation (7) all terms are measurable, though the experimental difficulties would be very great.

Porous Solids.

Bartell¹¹ has pointed out that a simple determination of the heat of wetting of a porous solid by a given liquid would suffice to determine its specific surface if once the free energy change per cm.², together with its temperature coefficient, were known with certainty. Whilst, however, he and his collaborators measured the heats of wetting by plunging the vapour-free adsorbents into the experimental liquids, the free energy changes were measured by noting the pressures necessary to displace either air or a second liquid from the pores of a diaphragm of the material¹²; that is to say, in the presence either of the vapour of the experimental liquid, or of a second component. The two sets of data so obtained cannot, therefore, be comparable.

Such measurements as are available would suggest that when a solid adsorbent, already exposed to a saturated vapour, is plunged into the liquid, very little heat indeed is disengaged.¹³ This may mean either that the first of the two bracketed expressions in equation (7) is far more important than the second, or that the pores or cracks which contribute mainly to the total surface are too fine for the penetration of further molecules when their adsorbed films (whatever their nature) are fully developed.

The ability of a liquid to penetrate or soak into a porous solid affords no real criterion of its power to spread uniformly over a plane surface of the same material. The condition for the latter kind of spreading, if saturation conditions prevail, is that $\theta = 0$, or (*cf.* equation 1)

$$\gamma_{SV} \leq \gamma_{SL} + \gamma_{LV} \quad (8)$$

When the solid is highly porous, however, a large amount of liquid may be soaked in without materially increasing the liquid-vapour interfacial area; in cases where the increase is negligible the condition for spreading on the internal surfaces of the solid becomes

$$\gamma_{SV} > \gamma_{SL}$$

and equation (1) shows that penetration and capillary rise will occur so long as $\theta < 90^\circ$.

¹¹ Bartell and Fu, *Colloid Symposium Annual*, 1930, 7, 135.

¹² Bartell and Osterhof, *Colloid Symposium Monograph*, 1928, 5, 113.

¹³ Parks, *Phil. Mag.*, 1903, 5, 517; Ray and Ganguli, *Trans. Faraday Soc.*, 1934, 30, 2 (silica gel); Katz, *Proc. Akad. Wetensch. Amsterdam*, 1923, 26, 549 (animal charcoal).

It is commonly believed, on good evidence, that supersaturation effects with vapours are more difficult to obtain in the presence of roughened or porous surfaces than in vessels of which the walls are uniformly smooth. That a porous solid need not *necessarily* provide nuclei of condensation, however, is proved by an experiment, described in the paper which follows,¹⁴ in which wood charcoal was found unable to condense bulk liquid phase from the supersaturated vapour of methyl alcohol. Since the charcoal, even if already exposed to the saturated vapour, was found to soak up large additional quantities of the liquid by capillary rise, it follows that $\theta < 90^\circ$. A liquid droplet resting in a cavity would have a concave meniscus under these conditions, and so be capable of indefinite growth. Unless one ascribes to it rather a special structure it is difficult to escape the conclusion that a porous solid, if its degree of wettability be sufficient to give rise to capillary condensation, should fill up *completely* with liquid when exposed to the saturated vapour. We have satisfied ourselves that this does not happen with wood charcoal.

Summary.

The work $W = \gamma_{LV}(1 + \cos \theta)$, which is done per unit area when a solid and a liquid are pulled apart, is to be distinguished from the work of adhesion as commonly understood, and is largely determined by the nature and properties of the adsorbed phase formed from the saturated vapour. Where supersaturation effects can occur in the vapour phase in the presence of the solid surface, the wetting angle θ is finite, and the aggregational state in the adsorbed phase must differ in some way from that in the bulk liquid.

The heat of immersional wetting is given by $F_L - T \frac{dF_L}{dT}$ (F_L = surface energy lowering on immersion) and is to be distinguished from the total heat of adsorption at saturation.

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¹⁴ Bangham and Razouk, *loc. cit.*; ⁹ cf. also the remarks of Williams, *Trans. Faraday Soc.*, 1914, 167.

THE WETTING OF CHARCOAL AND THE NATURE OF THE ADSORBED PHASE FORMED FROM SATURATED VAPOURS.

By D. H. BANGHAM AND R. I. RAZOUK.

Received 19th August, 1937.

Whilst most authorities are agreed that capillary condensation plays a minor rôle in adsorption by charcoal,¹ opinions differ as to whether it is generally absent, or whether it comes into play only very near saturation. McBain,² who favours the former view, points out that whereas exposure to vapours is found to cause an expansion of charcoal, the volume change, if any, to be expected at the onset of capillary condensation would be a

¹ E.g., Polanyi, *Trans. Faraday Soc.*, 1932, 28, 316; *Physikal. Z. der Sowjet*, 1933, 4, 144; McBain, *The Sorption of Gases by Solids*, 1932, *passim*.

² *Op. cit.*, 148.

contraction. This view is almost certainly correct. Nevertheless, as the hygrometric properties of hair have been explained by others³ in terms of capillary condensation in intermicellar spaces, there remained sufficient ambiguity to render further experiments desirable.

Except that its expansion is isotropic,⁴ and that it is more sensitive to organic vapours than to water, the swelling of charcoal is an effect very similar to the lengthening of hair and other natural fibres of which use is made in hygrometry. For each vapour there is a well-defined and reproducible *saturation* value of the expansion, which decreases slightly with rise of temperature. According to the evidence of the adsorption-expansion-pressure data, the expansion is directly proportional to the surface free energy lowering of the charcoal.⁵

It has been observed by us that if charcoal, already swollen to the maximum by exposure to the saturated vapour of, say, methyl alcohol, is then immersed in the liquid, a slight but appreciable *further* expansion occurs. This result is in harmony with the conclusion already drawn from expansion-adsorption data, that the films formed even from the saturated vapour of methyl alcohol may be "gaseous" or at least have properties different from the liquid in bulk.⁶ Nevertheless it seemed to us advisable to seek confirmation of this point by experiments designed to show under what conditions the charcoal could be made to fill any or all of its macropores with liquid. This course was urged: (1) by the fact that in the extensometric experiments the adsorption measurements, made by a volumetric method, had necessarily stopped short of actual saturation; (2) on account of the widely-held opinion that a rough surface, especially if gas-free, would necessarily provide nuclei of condensation for the bulk liquid; and (3) on account of the possible bearing of the results on the controversial question as to whether "elastic" or lyophilic gels reach the same equilibrium in the saturated vapours as they do in the liquid.⁷

Experimental.

The charcoal used by us was an inactive willow-wood charcoal of low ash-content, which previous experiments had shown capable of adsorbing, at pressures bordering on saturation, quantities roughly equivalent to 0.15 c.c. of the bulk liquids per g. The total pore volume, as determined from the "block" density, was much greater, about 2.6 c.cs. per g. Microscopic examination showed the pores to consist mainly of continuous and nearly cylindrical channels of about 2×10^{-3} cm. average radius, which had been, originally, the water conducting vessels of the woody tissue.

Series I: Experiments with Saturated Vapour.—Rectangular prisms of this material, about 15 cms. long, were suspended from spring balances of the McBain-Bakr type, so that their long axes (and the axes of their conducting pores) were vertical. After prolonged vacuum heating in an all-sealed-glass apparatus, these blocks were then exposed to the

³ Whipple, *Proc. Physical Soc.*, 1922, 50 (General Discussion on Hygrometry); cf. also Hedges, *Trans. Faraday Soc.*, 1926, 22, 178; Speakman, *Proc. Roy. Soc.*, A, 1931, 132, 167.

⁴ Meehan, *Proc. Roy. Soc., A*, 1927, 115, 199.

⁵ Bangham and Fakhoury, *J. Chem. Soc.*, 1931, 1324; Bangham, Fakhoury and Mohamed, *Proc. Roy. Soc., A*, 1932, 138, 162.

⁶ Bangham, Fakhoury and Mohamed, *ibid.*, 1934, 147, 152; the term "gaseous" is used here to denote an analogy not with three-dimensional gases, but rather with the gaseous monolayers formed, e.g. by the esters of the straight chain dicarboxylic acids at the surface of water.

⁷ See, for example, Katz, *Trans. Faraday Soc.*, 1933, 29, 279.

saturated vapours of different organic liquids which had been carefully fractionated and freed from dissolved gases. Excess of the liquid, similarly purified, was then distilled into the containing tubes.

Whether these systems were completely immersed in a thermostat for a period of weeks, or whether they were allowed to undergo the much wider fluctuations of room temperature (so that the charcoal must at times have been colder than either the walls of the container or the bulk liquid itself), the macropores of the charcoal remained obstinately empty. It is true that a slow and irregular increase in weight was observed, over and above that due to the adsorbed films; since, however, visible drops of liquid condensed on the suspending wires, and were observed from time to time to trickle down on to the charcoal, it appears highly probable that this increase (which did not exceed 0.15 g. per g. after a fortnight's exposure) was not due to direct condensation in the pores of the charcoal.

Series II: Capillary Rise.—By sealing to the blind end of the containing vessel a bent tube leading to a mercury reservoir (Fig. 1) it was made possible to vary the level of the bulk liquid at will. When raised to touch the base of the charcoal, the liquid rose more or less rapidly into the macropores, causing a large increase of weight. If at any stage its level was lowered again, the liquid broke cleanly away from the charcoal, which was left entirely free from hanging drops; this was true of all the liquids used. Advantage was taken of this fact to obtain time observations under more accurate conditions than if the lower end of the charcoal had been left floating in the liquid. The results of these rate-of-rise experiments were fairly concordant so long as the same charcoal block was always used, but they are not given here in detail because different blocks with the same history and apparently much the same macropore diameter were found to behave rather differently. Nevertheless the results are of comparative interest where the same charcoal block was used throughout.

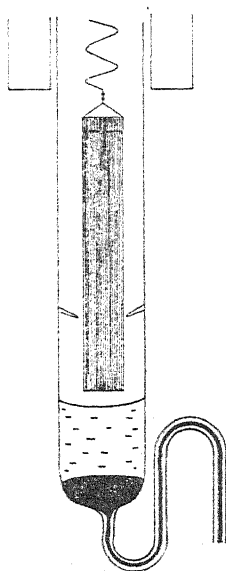


FIG. 1.

The analysis of Washburn⁸ shows that the distance of penetration in time t of a liquid entering a horizontal capillary of radius r under the influence of surface tension forces to be given by

$$l = \sqrt{\frac{2\eta}{tr\gamma_{LV}\cos\theta}} \quad (1)$$

where l is the distance of penetration, γ_{LV} the surface tension of the liquid, θ the angle of contact, and η the coefficient of viscosity. Disregarding the retarding influence of gravitation, the gain in weight due to capillary rise should therefore be proportional to the square root of the time. If the wetting angles be assumed zero, calculation shows that penetration of tubes 2×10^{-3} cm. radius should be so rapid with most common liquids as to fill tubes 15 cms. long in a matter of a minute or so; and that the volumes of water, benzene, methyl alcohol, and carbon tetrachloride sucked up in a given intermediate time should be in the ratios

$$\text{H}_2\text{O} : \text{C}_6\text{H}_6 : \text{CH}_3\text{OH} : \text{CCl}_4 = 1 : 0.76 : 0.71 : 0.60.$$

Experiments with these four liquids gave some results in rough general agreement with the square root relationship, though accurate and con-

⁸ Washburn, *Physic. Rev.*, 1921, 17, 276; cf. Rideal, *Phil. Mag.*, 1922, 44, 1154.

cordant values of the proportionality constant were not obtained. In all cases the rate of rise was slower than would be expected on the basis of a zero wetting angle, and with water and methyl alcohol it was very much slower indeed. But whether after an hour or so (benzene, carbon tetrachloride) or after a matter of days (methyl alcohol) or of weeks (water) the charcoal blocks in all cases eventually filled themselves to their full capacity.

If it could be assumed that the macropores were cylindrical vessels with smooth walls, the data obtained in these experiments could clearly be made to yield valuable quantitative information as to the angles of contact. For instance, since water was found to rise at least 15 cms. in capillaries of the dimensions stated, it would appear at first sight that $\cos \theta$, calculated from the equation

$$\gamma_{LV} \cos \theta = \frac{1}{2} g r h \rho \quad (2)$$

(where g = acceleration due to gravity, h = height, ρ = density) cannot have been much less than 0.2. The very slow rate of rise, on the other hand, would suggest that $\cos \theta$ is much smaller even than this. The two results are readily reconciled when we consider that in the large capillaries the edge of the meniscus must rise alternately over projecting angles which would delay its advance,⁹ and over the mouths of cracks and cavities which may already be wetted if the level in the main tube is nearing the limit of its rise against gravity.

The slow rate of penetration shown by methyl alcohol is in complete contrast to the behaviour of this liquid towards vapour-free charcoal; when a piece of the latter, recently baked out, is thrown into methyl alcohol, penetration is often so violent as to cause fracture. The difference of behaviour is clearly due to the surface pressure exerted by the adsorbed film, which opposes the advance of the liquid.

Series III: Experiments with Supersaturated Vapour.—In this series, small weighed blocks of charcoal were placed immediately under a wide jet from which air supersaturated with the vapour of methyl alcohol was issuing rapidly into the air. In no case were the macropores found to fill up, even though, in some experiments, the space around the jet was partly enclosed by glass tubing and filter paper, both of which became dripping wet in the course of the run.

Films of carbon deposited on glass slides by holding them over the luminous gas flame were found to behave quite differently, and afforded, as they caused immediate condensation, a very sensitive test for the supersaturation of the vapour. The glass slides without the deposit were found to be much less sensitive.

Discussion.

The above experiments show conclusively that even under saturation conditions the films formed on the surface of the wood charcoal cannot properly be described as liquid, and the fact that the charcoal exposed to saturated vapour expands still further on immersion is thus explained. Whilst caution is always necessary in generalising from results obtained with a particular charcoal, we would emphasise the theoretical importance of even a single negative result along the lines of the experiments of Series III, for there are a number of adventitious circumstances which could cause filling of the pores. The presence of much hygroscopic ash would give rise to increased wettability by water, and is known to affect materially the water relations of a charcoal;¹⁰ dense hydrocarbon

⁹ Coghill and Anderson, *U.S. Bureau of Mines, Tech. Paper*, 1923, 262; Adam, *Physics and Chemistry of Surfaces*, 1930, 193.

¹⁰ Coolidge, *J. Amer. Chem. Soc.*, 1927, 49, 708; Allmand, Hand and Manning, *J. Phys. Chem.*, 1929, 33, 1694; Bartell and Smith, *Ind. Eng. Chem.*, 1929, 21, 1102.

residues could act as nuclei of condensation for benzene and other organic liquids. Perhaps the much greater wettability of lamp-black by organic liquids is due to the latter cause, but another possibility is that condensation took place at the areas of contact between the carbon particles and the glass. The capillary rise experiments show that given one or more centre of condensation in immediate contact with the charcoal, the liquid will penetrate the latter until the whole pore-space becomes filled. For this reason the appearance of liquid drops and films in glass or metal vessels containing charcoal powder cannot be considered as evidence of direct condensation in the pores of the latter; the unattainable ideal would be to have the charcoal out of contact with all other bodies.

The penetration experiments also explain the failure of some earlier attempts of the authors to float charcoal particles on liquids in the absence of air, and in the presence of the saturated vapours. Only with water would a small fraction of the particles remain afloat for an appreciable time; with other liquids small particles sank immediately.

It is not suggested that the inability of the films to act as condensation nuclei implies necessarily a very wide divergence of properties between them and the bulk liquids. The fact alone that as saturation is approached the quantities of different vapours adsorbed more and more nearly represent equal volumes of the liquids is sufficient to discount such an extreme view. Moreover it has been shown by Lindau¹¹ that the ratios of the slopes of the logarithmic isotherms of different vapours approach values demanded by the capillary condensation theory as the vapours become saturated. But there can be no doubt, from the evidence given here, that the adsorbed vapour phase and bulk liquid must be regarded as distinct thermodynamic entities, separated in general by a discontinuity. The interpretation of this statement (which applies to polymolecular films)¹² in terms of theories of molecular aggregation must await more precise information as to the structure of liquids.

Calculation of Surface Free Energy Lowering from Coolidge's Adsorption Data.

In the preceding paper¹³ it was shown that the reduction of surface energy which accompanies the immersional wetting of a solid comprises two terms: (1) A decrease F_s due to adsorption of the saturated vapour, which is given by

$$F_s = RT \int_{p=0}^p \bar{\Gamma} d \log_e p \quad . \quad . \quad . \quad (3)$$

where $\bar{\Gamma}$ is the number of moles adsorbed per cm.² at variable pressure p , p_0 is the saturation pressure, and R and T have their usual meanings; and (2) the decrease taking place when the vapour phase is replaced by bulk liquid; this is $\gamma_{LV} \cos \theta$, where γ_{LV} is the surface tension of the liquid. The experiments which have been described do not suffice for the measurement of θ , but the information they give, which may be summarised in the statement

$$90^\circ > \theta_{H_2O} \gg \theta_{CH_3OH} \gg \theta_{CCl_4}, \theta_{C_6H_6} > 0^\circ$$

is none the less valuable, for it sets a rough upper limit to the second term of the surface energy decrease.

¹¹ Lindau, *Koll. Z.*, 1932, **60**, 253.

¹² Bangham, Mosallam and Saweris, *Nature*, 1937, **140**, 237.

¹³ *Trans. Faraday Soc.*, 1937, **33**, 1459.

With porous solids equation (3) permits the first of the two terms to be calculated only if the specific surface is known. Replacing Γ , the adsorption in moles per cm.² by s , its value expressed in g. per g. of adsorbent, we obtain

$$F_s = \frac{RT}{M\Sigma} \int_{p=0}^{p=p_0} s d \log_e p \quad (4)$$

where Σ is the specific surface, and M the molecular weight of the vapour. By taking advantage of the fact that the films of the lower alcohols adsorbed on mercury, and on the wood charcoal of Bangham, Fakhoury and Mohamed appeared to obey the same equation of state, Σ has been calculated for this charcoal, and a value assigned to the proportionality factor for converting the measured expansions into dynes per cm. of

TABLE I.

F_s = surface pressures (dynes) at saturation.

A_s = area per single molecule at saturation (Angström units).

Σ = apparent area of film per g. of charcoal (m.²).

1.	2.	3.	4.	5.	6.
	Coolidge's Steam-Activated Charcoal; F_s by Integration.			Unactivated Wood Charcoal II of B., F., and M.; F_s from Expansion Data; $\Sigma = 180 \text{ m}^2$.	
	Σ .	F_s .	$F_s A_s$.	F_s .	$F_s A_s$.
Benzene, 0° C. . . .	510	—	—	219*	3500
Benzene, 88.6° C. . .	—	172	3010	—	—
Methyl alcohol, 0° C. . .	420	—	—	202*	1240
Methyl alcohol, 59.5° C. .	—	199	1320	—	—
Water, 23° C. . . .	558	—	—	77	310
Water, 0° C. . . .	—	88	352	—	—

* Decreases slowly with rise of temperature.

surface pressure.¹⁷ It will now be shown that on the steam-activated charcoal used by Coolidge, also, much the same equations of state were obeyed in comparable cases.

Rough calculations have been made from Coolidge's data,¹⁴ using equation (4), and assuming Σ for his charcoal equal to 180 m.² (the value found for charcoal II of Bangham, Fakhoury and Mohamed)¹⁵ multiplied by the ratio of the saturation adsorption values of the two charcoals at equal temperatures. The values of F_s so obtained are set out in column 3 of Table I, and are to be compared with those derived from expansion measurements given in column 5.

The results obtained by integration cannot be regarded as more than tentative, because of difficulties in extrapolating the isotherms to zero

¹⁴ Coolidge, *J. Amer. Chem. Soc.*, 1924, 46, 596; the special merit of these data lies in the precision of the low pressure measurements, made with a modified McLeod gauge, and checked by a quartz suspension guage.

¹⁵ In Table I, the abbreviation B., F., and M. has been used for Bangham, Fakhoury and Mohamed.

pressure, which indeed become insuperable when lower temperatures are considered; moreover, the three values of Σ assigned to Coolidge's charcoal are in poor agreement. But notwithstanding these reservations it is remarkable that there should be tolerable agreement in the values of F_s calculated by the two methods. Even more significant is the rough agreement between the values of the product $F_s A_s$, A_s being the area per molecule at saturation: for, unlike those of F_s , the values of $F_s A_s$ are independent of the specific surface assigned to Coolidge's charcoal.

In a similar manner, a measure of the surface energy lowering F at any desired relative pressure p/p_0 is obtained by means of the relation

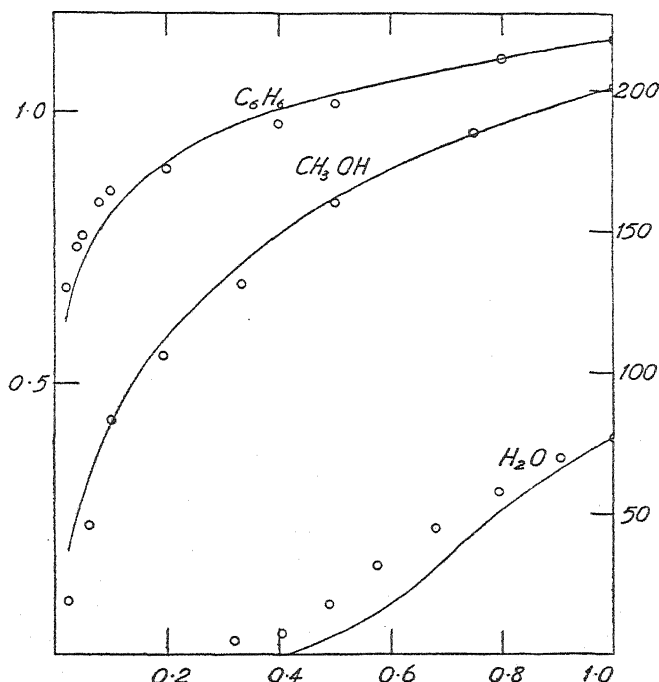


FIG. 2.—The curves are graphs of $\text{const.} \times \int_p^{p_0} T d \log p$ (ordinates) plotted against the relative pressure (abscissae) using Coolidge's 0°C. data for activated coconut charcoal. The points show per cent. linear expansion measurements made with inactive charcoal II of Bangham, Fakhoury, and Mohamed (scale on left). A scale of dynes is given on the right.

$$F = \frac{RT}{M\Sigma} \int_p^{p_0} d \log_e p \quad (5)$$

which, like equation (4) above, is an expression of the Gibbs thermodynamic adsorption relation in integrated form, applied to a film of area Σ . A more direct method for comparing the two sets of values for F at intermediate pressures, however, is to evaluate the integral

$$\int_p^{p_0} d \log_e p$$

from Coolidge's data, and then to compare the results (which should be proportional to $F_s - F$) with expansion differences measured over the same intervals of relative pressure. This has been done in Fig. 2, where

values of this integral, derived from Coolidge's 0° C. data are plotted as ordinates against the relative pressures as abscissæ. The terminal points of the curves at $p/p_0 = 1$ have been made to coincide with the saturation adsorption values, and the scale has been so chosen as to give the best agreement with the points representing the measured expansions with benzene and methyl alcohol.¹⁶ Extrapolation of the isotherms to zero pressure is thus avoided, and the order of agreement obtained with a single adjustable parameter is remarkable. The scale of dynes shown on the right of the diagram is related to the scale of percentage linear expansions on the left by the proportionality factor found¹⁷ with the aid of Cassel and Salditt's data¹⁸ for adsorption on mercury.

Isotherms of Water.

The fact that the data for water plotted in Fig. 2 show a lower order of agreement is not surprising in view of its very varying behaviour towards different charcoals.

Especially in dealing with water, the usefulness of equation (5) for deriving a two-dimensional equation of state is somewhat impaired by doubt as to whether the Gibbs thermodynamic equation, from which it is developed, can be valid when hysteresis phenomena are observed. Should the hysteresis be due to a suspended phase change, the complete breakdown of the Gibbs relation could not be assumed, for metastable phases are governed by the same forms of thermodynamic relationship as stable ones. At all events, no exception can be taken to the application of equation (5) to Coolidge's data for water adsorbed on ash-free *sugar* charcoal,¹⁹ where almost complete reversibility was attained.²⁰ These data are probably more truly representative than most of the charcoal-water system (Coolidge).

The general form of the 20° C. isotherm for water on this charcoal is shown in Fig. 3A, the abscissæ being values of $\log_{10} p/p_0$, and the ordinates fractions of the saturation adsorption. The isotherm rises sharply, almost with a discontinuity, at about half the saturation pressure. Since Henry's law was found valid at low pressures, the evaluation of the integral of equation (5) presents no difficulty until this steeply rising section is reached. It is convenient to represent the results of the integration in the form of a graph of FA against F (A = area per molecule), for it happens that the uncertainties arising from the manner of drawing the semi-log isotherm curve through the point of inflexion are almost without effect on the slope and position of the rising branch of the graph so obtained (Fig. 3B). To assign a scale of dynes to the diagram, it has

¹⁶ At pressures below 1 mm., the adsorption and expansion measurements of Bangham, Fakhoury and Mohamed (who used an ordinary mercury manometer) are relatively more accurate than those of the pressure. For this reason, in preparing the graphs of Fig. 2, the expansions corresponding to the *lowest* relative pressures of benzene have been calculated indirectly from the expansion-adsorption data, the assumption being that the relative pressures at equal fractions of the saturation adsorptions would be equal; elsewhere the directly read pressures have been used in preference. The discontinuity associated with deviations from the Gibbs adsorption equation, found by B., F. and M. in the case of methyl alcohol at 0° C., occurred at pressures smaller than any plotted in the figure.

¹⁷ Bangham, *Proc. Roy. Soc., A*, 1934, 147, 175.

¹⁸ Cassel and Salditt, *Z. physik. Chem.*, 1931, 155, 299.

¹⁹ Coolidge, *J. Amer. Chem. Soc.*, 1927, 49, 708.

²⁰ For a discussion and justification of the use of equation (5) over the range of a change of phase, see Bangham, *Trans. Faraday Soc.*, 1937, 33, 805.

been assumed that the specific surfaces of the sugar charcoal and of the wood charcoal IIA of Bangham, Fakhoury and Mohamed (which behaved very similarly) lay in the ratio of the saturation adsorptions in the two cases. The points plotted in the same figure (3B) are derived from *expansion measurements* with wood charcoal IIA,²¹ using the same proportionality factor as previously. The agreement here is very striking. The film, which is clearly gaseous at the lowest pressures where Henry's law is obeyed,²² undergoes condensation as the adsorption increases, FA decreasing sharply whilst F remains nearly constant. This is in the region where, in Fig. 3A, the isotherm bends sharply away from the abscissa axis. When, however, the point of inflexion in the latter graph is passed, F increases again rather sharply, giving rise to the rising arm

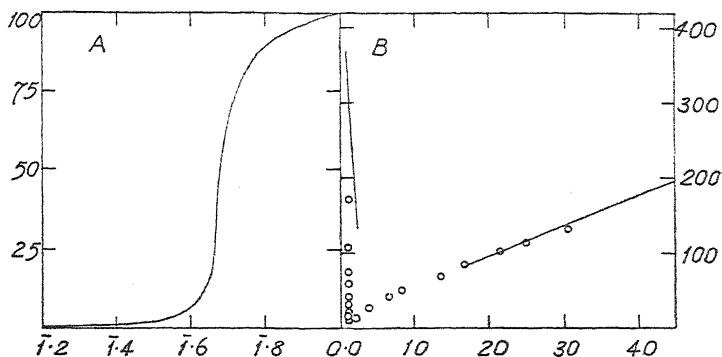


FIG. 3A.—Coolidge's isotherm for water adsorbed on sugar charcoal, $+20^{\circ}$ to -30° C.; abscissae, $\log_{10} p/p_0$; ordinates, per cent. of saturation adsorption.

FIG. 3B.—Abscissae, surface energy lowering F (dynes); ordinates, FA (ergs); curves are derived from Coolidge's data; the point circles from the expansion measurements of Bangham, Fakhoury, and Mohamed.

of the FA graph, which points back towards the origin. These characteristics are faithfully reproduced in the curve derived from the expansion data.

The designation of the condensed surface phase formed by water as a *liquid monolayer*²¹ is probably incorrect and misleading, and would be justifiable only if it were known that the charcoal in question is completely wettable by water. A parallel case is known to us where drops of the liquid fail to spread on a surface on which the adsorbed phase formed by the vapour is almost certainly a condensed one.

Summary.

From experiments in which wood charcoal of low ash-content was exposed to the saturated and supersaturated vapours of some common liquids, it is concluded that the adsorbed films formed are unable to act as nuclei of condensation for the bulk liquids. Experiments in which the rate of capillary rise was measured suggest that the wetting angle, in the presence of the saturated vapour, is fairly small for benzene and carbon tetrachloride, greater for methyl alcohol, and rather large in the case of

²¹ *Proc. Roy. Soc., A*, 1932, 138, 162.

²² Gibbs's adsorption equation requires that when Henry's law is obeyed, $FA = kT$ where k is the gas constant per molecule.

water. A new method is developed for finding the two-dimensional equations of state of adsorbed films on solids, which gives results in fair agreement with those derived from measurements of the expansion effect in charcoal.

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THE MAGNETIC SUSCEPTIBILITY OF THE $-\text{CH}_2-$ GROUP IN COMBINATION.

BY J. FARQUHARSON AND M. V. C. SASTRI.

Received 23rd August, 1937.

In the magnetic study of organic compounds the susceptibility of the $-\text{CH}_2-$ group has been used to a large extent as a standard. Pascal's¹ value has been used for the most part but recently its accuracy has been questioned.^{2,3} Pascal's value is $\chi_M = -11.86 \times 10^{-6}$; Bhatnagar, Mitra and Tuli² give a value of -11.355×10^{-6} . They studied homologous series of primary alcohols, acids, esters and aromatic hydrocarbons. The compounds they selected were the first few members of each series where any effect of the end group will be greatest and the value of $-\text{CH}_2-$ subject to errors. Cabrera and Fahlenbrach³ have made accurate measurements of the series of primary alcohols up to dodecyl alcohol. The molecular susceptibilities they obtained lie on a straight line when plotted against the number of $-\text{CH}_2-$ groups. They calculate a value for $-\text{CH}_2-$ of -11.48×10^{-6} . This value appears to us to be erroneous.

Experimental.

We have had occasion to examine the susceptibilities of the primary aliphatic acids in connection with an investigation of the effects of ring closure. The measurements were made on a Gouy type of apparatus using

Acid.	No. of $-\text{CH}_2-$	$-\chi \times 10^6$.	$-\chi_M \times 10^6$.
<i>n</i> -Butyric .	3	0.6253	55.07
<i>n</i> -Valeric .	4	0.6548	66.85
<i>n</i> -Caproic .	5	0.6730	78.14
<i>n</i> -Heptylic .	6	0.6900	89.74
<i>n</i> -Caprylic .	7	0.7053	101.60

a field of 5700 gauss and a sensitive chemical balance. The weighings were made by the method of swings. At least six measurements were made on each specimen, the average deviation from the mean never being more than 0.30 per cent. The accuracy of the results was increased by the fact that all the substances were liquids. Great care was taken in purifying the specimens. All glass-distilling apparatus was used. Resistance glass was used throughout as it was found that the storing of the acids in soft glass

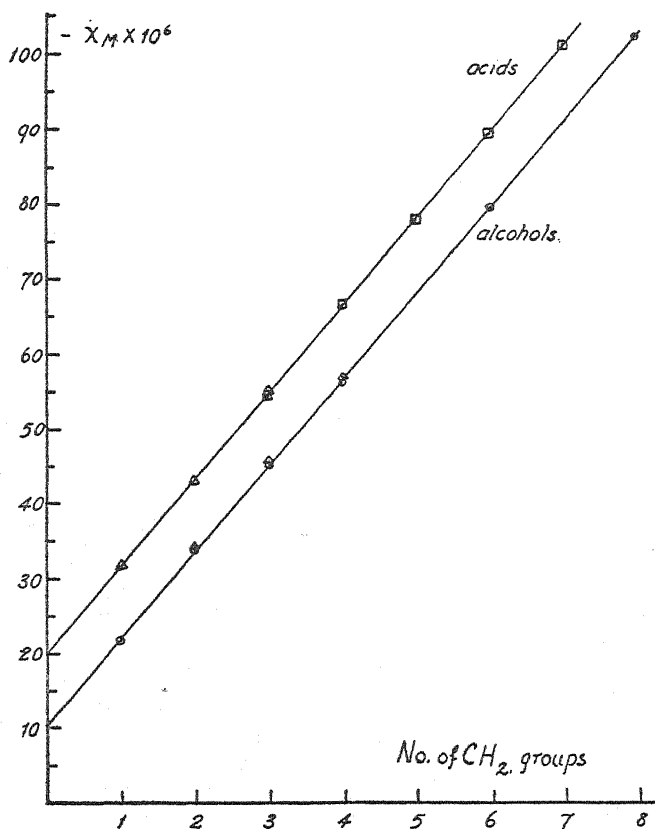
¹ Stoner, *Magnetism and Matter*, p. 469.

² Bhatnagar, Mitra and Tuli, *Phil. Mag.*, 1934, 18, 449.

³ Cabrera and Fahlenbrach, *Z. Physik*, 1933, 85, 568.

affected the results. The purity was checked by the density determinations, by refractive indices and by purifying until constant susceptibility was found. The values we obtain are shown in the Table above.

When these values are plotted on the same scale as those of Cabrera and Fahlenbrach and Bhatnagar, Mitra and Tuli as is done in the figure,



Magnetic Susceptibilities of Primary Acids and Alcohols.

- Cabrera and Fahlenbrach.
- △ Bhatnagar, Mitra and Tuli.
- Present Paper.

it will be seen that they are all in agreement and that we get two parallel straight lines. The equation for each straight line will be of the form

$$\chi_M = a \cdot n + b$$

where b is the intercept on the χ_M axis and is the value of the end groups, a is the susceptibility of $-\text{CH}_2-$ and n the number. Although they mention an equation of this type and draw the curve, Cabrera and Fahlenbrach find a value for b of -10.55×10^{-6} whilst the intercept is obviously -10.10×10^{-6} . By plotting the curves on a large scale we find the most probable value of b for the acids is -20.10×10^{-6} and

for the alcohols $10 \cdot 10 \times 10^{-6}$. By subtracting this value from the molecular susceptibilities of the individual acids we get $n\text{CH}_2$ and $-\text{CH}_2-$. Applying this method to our values for the acids we find $-\chi_M \times 10^6$ for CH_2 to be 11·657, 11·687, 11·608, 11·607, 11·643 giving a mean of $11 \cdot 64 \pm 0 \cdot 026$. The same method applied to Cabrera and Fahlenbrach's results for the alcohols we find a mean value of $11 \cdot 63 \pm 0 \cdot 11$. We consider that the most probable value for the susceptibility of the $-\text{CH}_2-$ group in combination is

$$\chi_M = -11 \cdot 64 \times 10^{-6}$$

Summary.

The present results along with those of others show that the susceptibility of $-\text{CH}_2-$ is $-11 \cdot 64 \times 10^{-6}$.

The authors wish to thank Professor D. H. Peacock for his advice and The University of Rangoon for research grants.

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THE EFFECT OF RING CLOSURE ON MAGNETIC SUSCEPTIBILITY.

BY J. FARQUHARSON AND M. V. C. SASTRI.

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Pascal¹ measured the magnetic susceptibilities of certain derivatives of polymethylenes with the object of deriving the constitutive factors for the various polymethylene rings. He considered his results to be in accordance with the Baeyer strain theory. This, however, must have been in a qualitative way only as his results show constitutive effects of the same magnitude for the trimethylene and hexamethylene rings although these are very different as regards strain and stability. The substances chosen by Pascal for his investigation were very dissimilar in constitution, for example, diethyl cyclopropane dicarboxylate and cyclohexane were used to make a comparison between the tri- and hexamethylene rings. These substances are not strictly comparable and errors probably arose in Pascal's work when he corrected for the other groups present in order to arrive at values for the different rings. This difficulty has been obviated by investigating derivatives of the polymethylene series and the related open chain compounds in order to get a measure of the effects of ring closure. For the most part the comparisons are confined to the monocarboxylic acids.

Experimental.

The normal fatty acids, cyclohexane carboxylic acid, cyclo-hexanone, cyclohexanol and normal hexane were purchased in the purest available

¹ Pascal, *Compt. Rend.*, 1925, 180, 1596; 181, 656.

form from reliable firms. Each was subjected to purification. The other substances investigated were prepared in the laboratory here as follows:

Cyclohexane monocarboxylic acid.—By the method of Perkin and Carpenter² with but slight modification.

Cyclobutane monocarboxylic acid.—Ethyl malonate (77 g.) and trimethylene bromide (50 g.) were added to absolute alcohol in which sodium (11 g.) had been dissolved. The reaction was vigorous and was completed by boiling for two hours. The dicarboxylic ester after separation was hydrolysed by alcoholic potash and the dicarboxylic acid extracted with ether. By heating this acid, the monocarboxylic acid was obtained. This was

TABLE I.

Substance.		t° .	D_{40}^{20} .	$- \chi \times 10^6$.	$- \chi_M \times 10^6$.
<i>n</i> -Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	30	0.6532	0.8710	74.91
Cyclopropane carboxylic acid	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{COOH} \end{array}$	30	1.0804	0.5271	45.33
Cyclobutane carboxylic acid	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 - \text{CH}_2 \\ \\ \text{CH}_2 - \text{CH} \cdot \text{COOH} \end{array}$	30	1.0544	0.5816	58.16
Cyclopentane carboxylic acid	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \qquad \diagdown \\ \text{CH}_2 - \text{CH}_2 \qquad \text{CH} \cdot \text{COOH} \end{array}$	30	1.0510	0.6446	73.48
Cyclohexane carboxylic acid	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \qquad \diagdown \qquad \diagup \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \qquad \text{CH} \cdot \text{COOH} \end{array}$	30	1.0274	0.6499	83.24
Cyclohexane	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\ \qquad \diagdown \qquad \diagup \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \end{array}$	27.5	0.7735	0.8100	68.13
Cyclohexanol	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\ \qquad \diagdown \qquad \diagup \\ \text{CH}_2 - \text{CH}_2 - \text{CH} \cdot \text{OH} \end{array}$	30	0.9495	0.7330	73.30
Cyclohexanone	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{C} = \text{O} \\ \qquad \diagdown \qquad \diagup \\ \text{CH}_2 - \text{CH}_2 \end{array}$	29.5	0.9376	0.6320	61.98
Cyclopentanone	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{C} = \text{O} \\ \qquad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$	30	0.9480	0.6141	51.63

purified by treatment with sodium carbonate and acidifying, and then by distillation. 10 g. of a pure specimen were obtained.

Cyclopentanone.—By the careful distillation of an intimate mixture of adipic acid (10 pts.) and barium hydroxide (1 pt.).

Cyclopentane carboxylic acid.— Δ^1 Cyclopentene carboxylic acid was prepared from cyclopentanone by the method of Cook and Linstead.³ (The cyclopentanone cyanhydrin was prepared by the direct union of cyclopentanone and liquid hydrogen cyanide.) This acid was then reduced to cyclopentanone carboxylic acid by catalytic hydrogenation in the presence of platinum oxide. The method used for taking the measurements was as described in the preceding paper. The results are in Table I.

² Perkin and Carpenter, *J. Chem. Soc.*, 1899, 75, 921.

³ Cook and Linstead, *J. Chem. Soc.*, 1934, 958.

Discussion.

The Constitutive Effects of Polymethylene Rings.

The constitutive effects of the various polymethylene rings can be found simply by comparing corresponding open-chain and cyclic compounds. If χ_{cy} is the susceptibility of the cyclic compound, χ_{op} that of the open chain compound, then

$$\chi_{cy} = \chi_{op} - 2\chi_H + \lambda$$

where χ_H is the atomic susceptibility of hydrogen in combination and λ is the constitutive factor for the ring. Since all the susceptibilities are negative, that is diamagnetic, a positive value for λ will indicate a fall in diamagnetism and a negative value a rise in diamagnetism. Substituting in this expression the values for the cyclic compounds in Table I, the values for the open chain acids in the previous paper and the experimental value for hydrogen, $\chi_H = -2.82 \times 10^{-6}$, the constitutive corrections for the various rings are as found in Table II. The figure

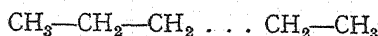
TABLE II.—CONSTITUTIVE CORRECTIONS FOR POLYMETHYLENE RINGS.

No. of C Atoms in the Ring.	Substances Compared.	$-\chi_M \times 10^6$.	λ	
			Present Paper.	Pascal.
3	$\left\{ \begin{array}{l} n\text{-Butyric acid} \\ \text{Cyclopropane carboxylic acid} \end{array} \right.$	55.07 45.33	+ 4.1	+ 3.6
	$n\text{-Valeric acid}$	66.85		
4	$\left\{ \begin{array}{l} \text{Cyclobutane carboxylic acid} \\ n\text{-Caproic acid} \end{array} \right.$	58.15 78.14	+ 3.05	+ 1.3
5	$\left\{ \begin{array}{l} \text{Cyclopentane carboxylic acid} \\ n\text{-Heptoic acid} \end{array} \right.$	73.48 89.74	- 0.98	+ 0.3 - 0.1
6	$\left\{ \begin{array}{l} \text{Cyclohexane carboxylic acid} \\ n\text{-Hexyl alcohol}^4 \end{array} \right.$	83.24 79.81	+ 0.86	+ 3.0 + 3.3 + 3.0
	$\left\{ \begin{array}{l} \text{Cyclohexanol} \\ n\text{-Hexane} \end{array} \right.$	73.30 74.91	+ 0.87	
	$\left\{ \begin{array}{l} \\ \text{Cyclohexane} \end{array} \right.$	68.13	+ 1.14	

employed for hydrogen is found by subtracting the susceptibility of carbon, which is well established as -6.00×10^{-6} , from χ_{CH_2} found in the preceding paper and dividing by two.

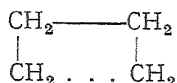
The Effect of Ring Closure on Diamagnetic Susceptibility.

When a saturated open chain compound of the type ;



undergoes ring closure forming the corresponding saturated cyclic compound ;

⁴ Cabrera and Fahlenbrach, *Z. Physik*, 1933, 85, 568.



the following structural changes take place ;

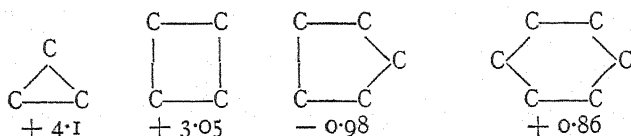
- (1) The loss of two atoms of hydrogen,
- (2) The loss of two (C—H) linkages,
- (3) The formation of an additional (C—C) link, and
- (4) The formation of a ring of carbon atoms which may give rise to

changes in molecular structure such as distortion of the tetrahedral symmetry of the carbon atoms, a change in the length of the (C—C) link, multiplanarity of the molecule, etc.

The difference in diamagnetism between the saturated cyclic compound and the corresponding saturated open chain compound must be due to all these changes. If it were possible to assess the magnetic changes which accompany the processes (1), (2), and (3) and the values so obtained were subtracted from the susceptibility of the open chain compound and there still remained a difference between this and the susceptibility of the ring compound then this difference must be due to the process (4) above. It is very difficult to obtain a correct assessment of the changes (1), (2), and (3) as there is no really reliable method of calculating these.

Recently Gray and Cruickshank ⁵ have developed a method by which these quantities may be calculated. This involves the use of theoretical standards for which they use Pauling's ⁶ values for atoms and ions. These values of Pauling are only approximate and must give rise to errors in susceptibilities calculated from them. However, in place of any better method, this can be used to give an indication of the magnitude of the effects (1), (2) and (3), for in the examples so far cited by Gray and Cruickshank the method gives correct results. In the present paper the total of the three effects has been calculated by considering the difference between two CH₃-groups and one —CH₂—CH₂— group and is found to be $(2 \times 14.46) - 23.28 = 5.64$. The figure obtained in this way is exactly twice the value for the hydrogen atom in combination and is added evidence that the values of λ which have been found are effects really due to differences in the magnetic properties of straight carbon chains and the carbon rings of the cyclic compounds, that is, are due to ring closure.

The Constitutive Corrections for the Polymethylene Rings.



A possible approach to an explanation of these figures is to consider the rise or fall in diamagnetism of the molecule as resulting from a change in the value of the carbon atom when situated in a ring. For example, in the case of the cyclo-propane compound, instead of introducing the correcting constant of 4.1 for the ring, the observed value can be accounted for by attributing to the carbon atom in the cyclopropane ring a susceptibility of $6 - \frac{4.1}{3} = 4.66\bar{3}$ instead of the value 6.0 appropriate for

⁵ Gray and Cruickshank, *Trans. Faraday Soc.*, 1935, **31**, 1491.

⁶ Pauling, *Proc. Roy. Soc., A*, 1927, **114**, 181.

straight chain compounds. The susceptibility of carbon in a polymethylene ring will thus be given by,—

$$\chi_0' = \chi_0 - \frac{\lambda}{n}$$

where χ_0 is the normal susceptibility of the carbon atom and n is the number of atoms in the ring. Table III gives the values for carbon in the various rings:—

Consideration of the charge distribution in the trimethylene and tetramethylene rings shows that a fall in diamagnetism is to be expected. Geometrically the valency angles between the carbon atoms in polymethylene rings are shown to be as follows, 3-ring, 60° ; 4-ring, 90° ; 5-ring, 108° ; 6-ring, almost tetrahedral 109° . The small valency angles in the trimethylene and tetramethylene rings is likely to lead to a concentration of the electronic charge in the ring leading to a smaller effective radius and a fall in diamagnetism of the carbon atom. The very small distortion of the valency angles in the penta- and hexamethylene rings should have but little effect, and the susceptibility of the carbon atom in these rings should not be greatly different from the susceptibility in a straight chain compound. The fact that the susceptibility of carbon in the hexamethylene ring is less than in the pentamethylene and also less than in an open chain compound is probably connected with the relative rigidities of the structures. It is significant, too, that this

TABLE III.—SUSCEPTIBILITY OF CARBON IN POLYMETHYLENE RINGS.

	$-\chi' \times 10^6$.
Cyclopropane	4.63
Cyclobutane	5.29
Cyclopentane	6.20
Cyclohexane	5.84

result is in line with recent work on electron diffraction. Brockway⁷ gives values for the C—C distance in paraffin chains of about 1.52 Å. (C_2H_6 , 1.52; C_3H_8 , 1.52; C_4H_{10} , 1.51; C_5H_{12} , 1.53), in cyclopentane, 1.52, and in cyclohexane, 1.51. It is to be expected that here, where there is no large amount of strain in the ring, the carbon atoms of the molecule with the larger C—C distance would have a rather more diffuse negative charge distribution and therefore a greater diamagnetic susceptibility, so that carbon in the five-membered ring should be relatively more diamagnetic than carbon in the six-membered ring.

Summary.

1. The magnetic susceptibilities of compounds containing 3, 4, 5 and 6 membered carbon rings and the related open chain compounds have been measured.
2. Constitutive correcting constants calculated for the rings differ from those of Pascal. The effect of ring closure is to cause a fall in diamagnetism in each case except in the 5-ring where there is a rise.
3. The necessity for correcting constants is interpreted as being due to changes in the value of the susceptibility of the carbon atom when it is a member of different sized rings.

The authors wish to thank Professor D. H. Peacock for advice and the University of Rangoon for a research grant.

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⁷ Brockway, *Rev. Mod. Physics*, 1936, 8, 231.

THE ENERGY AND SCREENING CONSTANTS OF THE HYDROGEN MOLECULE.

BY C. A. COULSON.

Communicated by PROF. J. E. LENNARD-JONES.

Received 30th August, 1937.

1. Introduction.

The theory of the screening effect exercised upon one electron in an atom by the charge-clouds of all the other electrons, has been worked out in detail, and explicit rules are available for writing down at once an approximate wave-function, or orbital, for any given electron.^{1, 2} With molecules, however, the situation is more complex, and in this paper a discussion is given for the simplest of all molecules, H_2 and H_2^+ . It is found that whereas in the atomic problem, the screening may, to a first approximation, be described by one numerical constant, *vis.*, the effective central nuclear charge for the selected electron, in the molecule there are two distinct screening effects, one due to the different electrons, and the other to the presence of neighbouring nuclei, and that both of these screenings vary with the size and shape of the molecule. This makes a generalisation to other molecules very difficult, but the general form of the results will be unchanged in all homonuclear molecules such as O_2 , N_2 , Li_2 , etc.

In the course of the work it appeared that although the ground state of the H_2 molecule had been treated by many writers, the basis of solution had always been that of the original Heitler-London treatment,³ suitably modified and complicated, and that practically no published results were available from the viewpoint of molecular orbitals.⁴ In this paper, therefore, a critical comparison is made of the two theories, and of their predictions concerning the internuclear distance, dissociation energy and fundamental vibration frequency. Such a discussion is interesting because this molecule is almost the only one where it is possible to carry through both approximate solutions and to compare them with a nearly exact one; and further, an indication is given of the reliability of the two treatments for other more complex problems, which must be solved by approximate methods.

2. The Wave-Functions Used.

The wave-functions used are those which have often been described before, and we need not discuss them in detail. Thus, for the electron-pair calculations (*e.p.*) we write

$$\psi = \{\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)\}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\} \quad (A)$$

¹ Eckart, *Physic. Rev.*, 1930, **36**, 878.

² Slater, *ibid.*, 57; 1932, **42**, 33.

³ Heitler and London, *Z. Physik*, 1927, **44**, 455.

⁴ Mulliken, *Physic. Rev.*, 1932, **41**, 49.

in which $\psi_a(1)$ denotes the wave-function of electron 1, supposed centred around nucleus A. α and β denote the spin terms, which will usually be omitted, since they make no further contribution to the energy or the wave-functions. The notation for the various distances is made clear in Fig. 1, and we shall suppose that only atomic units (*a.u.*) are used throughout, so that the complete Hamiltonian is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \{1/r_{1a} + 1/r_{1b} + 1/r_{2a} + 1/r_{2b}\} + 1/r_{12} \quad (1)$$

Similarly, in the molecular orbital treatment (*m.o.*) we write

$$\psi = \phi(1)\phi(2)\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\} \quad (B\ 1)$$

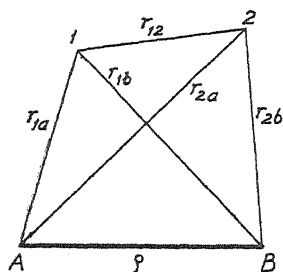


FIG. 1.

where $\phi(1)$ represents the molecular orbital for electron 1 in the field of the two nuclei and the second electron. Although more accurate forms for ϕ could be worked out, preferably using spheroidal co-ordinates⁵ we shall be content with the simplest type, the sum of atomic orbitals around nuclei A and B. This is Mulliken's LCAO approximation.⁶ We therefore put

$$\phi(1) = \psi_a(1) + \psi_b(1) \quad (B\ 2)$$

$$\text{and} \quad \psi = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) + \psi_a(1)\psi_a(2) + \psi_b(1)\psi_b(2).$$

It is well known that a better form of wave-function, which is a generalisation of both A and B, is obtained by taking different proportions of the 'homopolar' and 'ionic' terms, so that

$$\psi = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) + \lambda\{\psi_a(1)\psi_a(2) + \psi_b(1)\psi_b(2)\} \quad (C)$$

Wave-function C is neither pure *e.p.* nor pure *m.o.*, being intermediate between the two, since $\lambda = 0$ gives A and $\lambda = 1$ gives B. Weinbaum⁷ finds that at the equilibrium separation, λ is approximately equal to 0.25. To obtain even better results, of course, even this should be modified to allow for polarisation effects.⁷

It remains to decide what form shall be chosen for ψ . The present calculations are made upon the customary assumption that ψ is merely the atomic orbital of a 1s electron with, perhaps, a variable effective nuclear charge. Thus

$$\psi_a(1) = (c^3/\pi)^{\frac{1}{2}} e^{-cr_{1a}} \quad (2)$$

The exponent c will not as a rule be constant, but will depend upon the nuclear separation.

The advantage of wave-functions A, B and C over more complicated ones, such as those used by Coolidge and James⁵ which give equally good or even better, values for the energy, is that these functions are susceptible of a simple pictorial interpretation. Thus, in C, there are equal chances of finding electron 1 on nucleus A and electron 2 on nucleus B, as *vice versa*, and the chance of finding them both on either nucleus is λ^2 times as great; furthermore, when an electron is around nucleus A in the form ψ_a , it behaves just like an electron in the lowest state of an atom of nuclear charge c . With wave-functions expressed in spheroidal

⁵ Cf. James and Coolidge, *J. Chem. Physics*, 1933, 1, 825.

⁶ Mulliken, *ibid.*, 1935, 3, 375.

⁷ Weinbaum, *ibid.*, 1933, 1, 593.

co-ordinates, such an interpretation cannot be found, and the pictorial value of a screening constant is lost.

The *m.o.* solution depends essentially upon the solution of a one-electron problem, and this solution is fundamental to the subsequent discussion of screening constants. So let us first consider the H_2^+ ion in some detail. The wave-function for this molecule will be just that of a single molecular orbital B 2.

3. The Molecular Ion H_2^+ .

We consider one electron in the field of two fixed protons, whose separation is ρ ; the Hamiltonian for this problem is

$$H = -\frac{1}{2}\nabla^2 - 1/r_a - 1/r_b$$

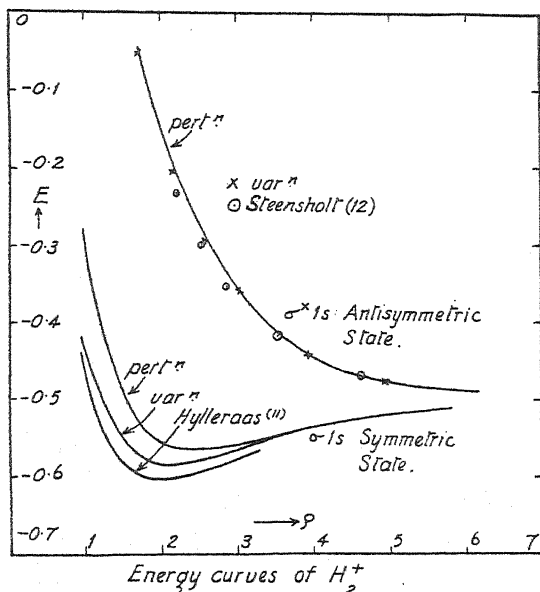


FIG. 2.

and when we use the wave-function B 2, defining ψ_a by equation (2), we find that the energy can be conveniently expressed in the form :

$$E = Ac^2 - Bc + 1/\rho \quad (3)$$

where A and B are known functions of a parameter t defined by

$$t = c\rho \quad (4)$$

There is no need to write down the explicit forms of A and B ; they are rather cumbersome and may easily be obtained, using the relation

$$E = \int \psi^* H \psi \, d\tau / \int \psi^* \psi \, d\tau$$

The crudest assumption to make concerning c is the one first made by Pauling,⁸ who assumed that $\psi_a(1)$ should be the wave-function for an isolated H atom, and hence that $c = 1$. The energy curve thus obtained is shown in Fig. 2 under the heading "Perturbation Method." If,

⁸ Pauling, *Chem. Rev.*, 1928, 5, 173.

however, for any given ρ , we find the best value of c , using the variational principle, we have to put $\left(\frac{\partial E}{\partial c}\right)_\rho = 0$

$$\text{i.e.,} \quad 2Ac + c^2\rho \frac{dA}{dt} - B - c\rho \frac{dB}{dt} = 0$$

$$\text{so that} \quad c = \frac{B + t \frac{dB}{dt}}{2A + t \frac{dA}{dt}} \quad (5)$$

This analysis is similar to that used by the writer⁹ in a discussion of H_3^+ . Thus c is found as a function of t , and, using equation 4, as a function

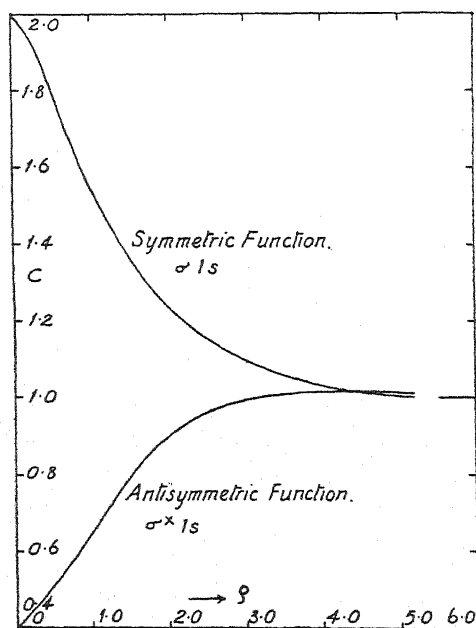


FIG. 3.—Nuclear screening for a single electron in H_3^+ . If the nuclear charges are each Z instead of unity, the same curves are obtained, plotting $Z\rho$ instead of ρ and c/Z instead of c .

and Steensholt¹² are shown for comparison.

It is instructive in Fig. 3 to trace the change-over from the separated-atom to the united-atom.⁴ In the symmetric case (B 2), when $\rho = \infty$, the orbital is a pure 1s hydrogenic orbital round either nucleus A or B, and when $\rho = 0$, it becomes a pure 1s hydrogenic orbital of the united nuclear charge 2. At the equilibrium separation, $c = 1.24$, indicating that the molecule partakes quite considerably of the united-atom characteristics. Mulliken has already suggested that an enhanced value of

of ρ also. The curves thus obtained, relating E and c to ρ , are shown in Figs. 2 and 3 ("Variational Method"). Finkelstein and Horowitz¹⁰ have used this type of wave-function, but only applied it at the equilibrium distance.

It is interesting here to insert the results for the wave-function corresponding to B 2, but which is antisymmetrical in the two nuclei. If we write

$$\phi = \psi_a - \psi_b \quad (B 3)$$

and perform similar calculations, the results shown in Figs. 2 and 3 are obtained. This energy curve is, of course, repulsive, but one of the (B 3) electrons together with one of the (B 2) electrons yield the famous Heitler-London repulsive state. In these two figures, the accurate calculations of Hylleraas¹¹

⁹ Coulson, *Proc. Camb. Phil. Soc.*, 1935, **31**, 244.

¹⁰ Finkelstein and Horowitz, *Z. Physik*, 1928, **48**, 118.

¹¹ Hylleraas, *Z. Physik*, 1931, **71**, 739.

¹² Steensholt, *ibid.*, 1936, **100**, 547; *Norske Vid-Akad. Avh.*, 1936, No. 4.

c may be a condition of firm binding. With the antisymmetric orbital (B 3), at $\rho = \infty$, we have either of two 1s hydrogenic orbitals, but at $\rho = 0$, a wave-function resembling a $2p$ orbital of the united-atom. Had we chosen our form for $\psi_a(1)$ better, in equation (2), we should have obtained a true $2p$ wave-function of the united-atom, since this is the limit of the lowest (B 3) orbital as $\rho \rightarrow 0$. It should be noted, however, that, using expression 2, we actually find

$$\psi_a - \psi_b \rightarrow \cos \theta \cdot e^{-cr} \quad \text{as } \rho \rightarrow 0$$

whereas, with better functions, we should have

$$\psi_a - \psi_b \rightarrow r \cos \theta \cdot e^{-cr} \quad \text{as } \rho \rightarrow 0.$$

The difference in the energies, however, is not great, and may be expected to be much less than the error in the wave-function.

At this stage reference must be made to two papers by Gordadse.²³ A wave-function similar to (B 2) was used for this problem, and the exponent c was varied to obtain the lowest energy. But the method of variation was incorrect, and his results are invalid. The two notations are equivalent if we notice that a, b, z, R and λ correspond to $A, -B, c, \rho$ and t respectively. Gordadse obtained equation (3) and then proceeded to vary c , keeping t constant, with the result that equation (5) became

$$c = B/2A.$$

This is an illegitimate variation, however, since $t = c\rho$, and if t is kept constant while c is varied, this implies that ρ is varied also, and we are no longer finding the lowest energy corresponding to a particular value of ρ . It follows that his equation (1.6) on page 289 should really be

$$R_{ik} = - \frac{2a + \lambda_{ik} \frac{da}{d\lambda_{ik}}}{b + \lambda_{ik} \frac{db}{d\lambda_{ik}}} \lambda_{ik}$$

instead of $R_{ik} = -(2a/b)\lambda_{ik}$. One result of his error is that the exponent c becomes less than unity for $\rho < 1.25$ a.u., whereas we know that as ρ tends to zero, c tends steadily to the "united-atom" value $c = 2$. (Fig. 3). It is not difficult to see, therefore, why his energy curve, as shown in Table I (p. 293) and Fig. 2 (p. 292) differs from the present writer's, and also from the single value obtained at $\rho = 2.0$ a.u. by Finkelstein and Horowitz¹⁰ with which it should agree, and with which the present writer is in complete agreement.

4. The Hydrogen Molecule.

In this calculation, using first the *m.o.* form, we employ wave-functions (B 1), (B 2) and equation (2). The energy can be put in the form

$$E = 2Ac^2 - 2Bc + Fc + 1/\rho \quad . \quad . \quad . \quad (6)$$

A and B are the same functions of the parameter t (equation (4)) as in the case of the ion, and F is another function of t , whose presence is due to the term $1/r_{12}$ in the Hamiltonian of equation (1). From here, we may follow the same two-fold development as in the last section, according as we allow c to vary, or put it equal to the nuclear charge, in this case unity.

Using first the perturbation method, with $c = 1$, the energy curve of Fig. 4 was obtained. A parabola was now passed through the three

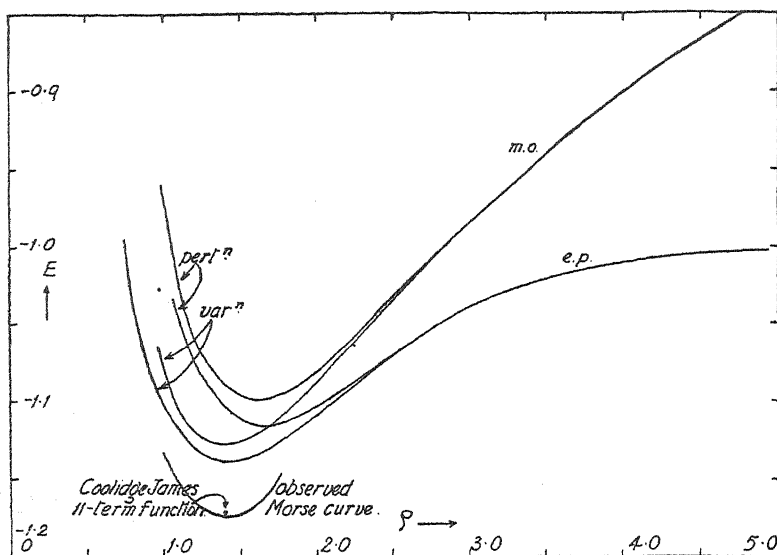


FIG. 4.— H_2 molecular energy curves.

TABLE ILLUSTRATING THE CONSTANTS OF THE HYDROGEN MOLECULE OBTAINED BY VARIOUS METHODS OF APPROXIMATION.

Method.	$r(\text{\AA})$.	Electronic Binding Energy (Volts).	$\tilde{\nu}$ (cm^{-1}).	α .
PERTURBATION.				
molecular orbital	0.850	2.681	4160	1.000
electron-pair (Sugiura ¹⁴)	0.80	3.2	4800	1.000
(corrected)	0.869	3.140	4080	1.000
VARIATION.				
molecular orbital	0.732	3.470	4580	1.197
electron-pair (Wang ¹⁵)	0.743	3.761	4900	1.166
(corrected)	0.743	3.761	4180	1.166
OTHER RESULTS.				
Hylleraas, <i>m.o.</i> interpolation ¹¹	0.70	3.6	—	—
Rosen, "Wang + Polarisation" ¹³	0.74	4.02	4260	1.19
Weinbaum, "Wang + Ionic" ⁷ Perturb.	0.90	3.21	—	1.00
Variation	0.749	4.00	4750	1.193
Weinbaum, "Wang + Ionic + Polarisation"	—	4.10	—	1.190
Coolidge-James, without r_{12} -terms ⁵	0.740	4.27	—	—
with r_{12} -terms	0.740	4.70	—	—
Eisenschitz and London, ¹⁶ second order perturbation	—	9.5	—	—
OBSERVED VALUES	0.740	4.72	4318	—

¹³ Rosen, *Physic. Rev.*, 1931, 38, 2099.

¹⁴ Sugiura, *Z. Physik*, 1927, 45, 484.

¹⁵ Wang, *Physic. Rev.*, 1928, 31, 579.

¹⁶ Eisenschitz and London, *Z. Physik*, 1930, 60, 491.

lowest points at $\rho = 1.5$, 1.6 and 1.7 a.u. and the equilibrium separation ρ_e , the fundamental vibration frequency $\tilde{\nu}$ and the dissociation energy D were obtained. They are given in the table, which also shows the results obtained when c is allowed to vary. (Variation Method.) In this case, equation (5) is replaced by the new equation

$$c = \left(2B + 2t \frac{dB}{dt} - F - t \frac{dF}{dt} \right) / \left(4A + 2t \frac{dA}{dt} \right). \quad (7)$$

Writing down the explicit forms of A , B and F , the value of c as a function of ρ is obtained, and is shown in Fig. 5. It is seen that the repulsion between the electrons tends to decrease c , i.e., to make the charge-cloud more diffuse. This is just what we should have expected, because the repulsion will tend to prevent the two electrons coming in close. Several values for the effective nuclear charge obtained by quite different methods, are also shown in Fig. 5, all of which lie around the theoretical curve just obtained. A

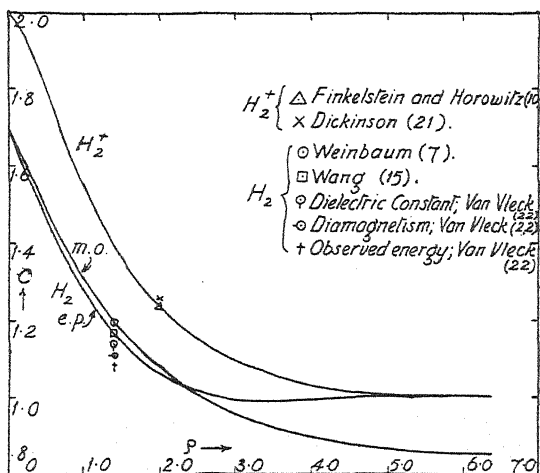


FIG. 5.

check upon the absolute minimum energy may be made by observing, similarly to Wang,¹⁵ that in these problems, the minimum value of \bar{E} , for all values of ρ , c and t , is the lowest value of

$$-(2B - F - 1/t^2)/8A$$

regarding this last expression merely as a function of t .

This last observation enables a possible source of error to be noticed. For in order to get ρ_e , D and $\tilde{\nu}$, a Morse curve was passed through three points near the minimum. The minimum is at about $\rho = 1.38$ a.u. and at first, the three points chosen were 1.25, 1.5 and 1.75 a.u. These gave a value $D = 0.1272$ a.u., whereas the absolute minimum, using the function above, must be at $D = 0.1282$ a.u. This error is by no means inappreciable (about 1 per cent.) but it was entirely eliminated when values $\rho = 1.25$, 1.375 and 1.5 were chosen to fit a Morse curve. We conclude that when passing such a curve through theoretical points, errors may easily creep in if we use too extended a range. The error in $\tilde{\nu}$ was worse; the first Morse curve yielded $\tilde{\nu} = 4794 \text{ cm}^{-1}$ and the second 4584 cm^{-1} . This is not altogether surprising since $\tilde{\nu}$ is very sensitive to small errors in the energy, and extreme care must be taken in its evaluation. In view of all this, a certain amount of doubt must be cast upon the precise results of Rosen¹³ who passed his Morse curve through the three points corresponding to $\rho = 1.0$, 1.5 and 2.0, and it is probable that his value of the fundamental frequency should be slightly reduced.

An *e.p.* treatment of the molecule has already been given, using wave-function A , by Heitler and London³ and by Sugiura¹⁴ who evaluated the interaction integral for which only an approximate value was obtained by the first authors, and by Wang.¹⁵ Sugiura used the perturbation method, placing $c = 1$ in equation (2), and Wang used the variation method, only applying it, however, at the equilibrium separation. Rosen¹³ subsequently obtained a relation between c and ρ similar to that just obtained in the *m.o.* analysis. The work of these authors has all been recalculated, and the results are shown in Figs. 4 and 5 and in the table. It appears, quite unaccountably, that the published figures of Sugiura are considerably in error, although his formulæ are all correct. This is rather unfortunate, because the figures have subsequently been quoted quite widely, and the corrected values fit the experimental observations rather worse than the old ones. Especially in the case of the frequency $\tilde{\nu}$, a large alteration is necessary; the new value (see table) is much more likely than the old one on *a priori* grounds; it will be noticed that in Sugiura's calculations, the curvature of the energy curve was too great, and that the new computation brings the value of $\tilde{\nu}$ on to a level with that obtained from the *m.o.* treatment. This is quite satisfactory, since we should expect that the potential curve would be flatter for the less accurate perturbation method than for the more accurate variational one.

Another interesting error was discovered, also connected with $\tilde{\nu}$, this time in the work of Wang. This author found that at the equilibrium distance ρ_e , the exponent c had the value 1.166, and in order to obtain a value for $\tilde{\nu}$ with the minimum of labour, he used this same value for c , even when ρ was slightly different from ρ_e .

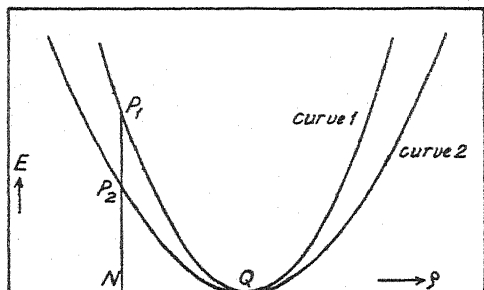


FIG. 6.

He found $\tilde{\nu} = 4900 \text{ cm.}^{-1}$, whereas an accurate analysis which allowed for the variation of c with ρ as shown in Fig. 5, gives $\tilde{\nu} = 4180 \text{ cm.}^{-1}$. This is

a huge error, caused, apparently, by only a very slight error in the wave-functions. We can show, however, that this large error is just of the order of magnitude to be expected. Fig. 6 shows the energy curves of the molecule near the minimum, obtained first by making $c = 1.166$ for all ρ (curve 1) and second by allowing c to vary with ρ , as indicated in Fig. 5 (curve 2). The second curve lies below the first curve, though they touch at the equilibrium point Q . If we express the energy near Q in the form

$$E = k(\rho - \rho_e)^2 \quad (8)$$

then $\tilde{\nu} \propto k^{\frac{1}{2}}$. Thus, if an error is made in k due to choosing curve 1 instead of curve 2, the error in $\tilde{\nu}$ is given by the relation $\delta\tilde{\nu}/\tilde{\nu} = \delta k/2k$. But, from Fig. 6, and equation (8),

$$\frac{\delta k}{k} = \frac{\delta E}{E} = \frac{P_1 P_2}{P_2 N}$$

If $\rho_N = 1.25$ it is found that P_1P_2 is about 0.0020 a.u. and PN is about 0.0055 a.u. so that

$$\delta\tilde{\nu}/\tilde{\nu} = 0.0020/2 \times 0.0055 = 1/5.5 \text{ approx.}$$

The actual figures obtained from the two curves are 4180 and 4900 cm^{-1} and these make

$$\delta\tilde{\nu}/\tilde{\nu} = 720/4180 = 1/5.7 \text{ approx.}$$

The agreement of the two ratios above shows conclusively that Wang's error is entirely due to taking the value of c appropriate to the equilibrium separation, and using it also for points nearby. And this analysis reveals yet once more how extremely susceptible the value of $\tilde{\nu}$ is to changes in the wave-function; to obtain a value which may be supposed to be reasonably accurate, one must obtain the best possible value for the energy at all points near the minimum, and not just the best at the minimum and almost the best elsewhere. It is curiously unfortunate that both the Sugiura and Wang values of $\tilde{\nu}$ are incorrect, since the published values give the impression that the *e.p.* method predicts a much greater curvature of the energy curve at the minimum than does the *m.o.* method, whereas in actual fact the two theories are almost equivalent.

This leads us to an interesting comparison of the results shown in the table. It has often been claimed that although the *m.o.* approximation is far superior with polar molecules since it automatically allows for any required degree of polarity, the *e.p.* approximation is better for cases of homopolar binding. This last claim is now seen to be less tenable than before. In fact, if we confine ourselves to the naïve perturbation treatment, the *m.o.* treatment gives a better value for ρ_e and $\tilde{\nu}$, though its energy value is half a volt worse than the *e.p.* method. If we use the more complex variational method, both are equally near the truth with ρ_e and $\tilde{\nu}$, and the *m.o.* energy is wrong by 1.25 volts, the *e.p.* energy by 1.0 volts. This is hardly justifiable ground for rejecting the *m.o.* method completely, for all cases of homopolar binding, as many authors have done.

It is interesting to note that over a wide range of ρ , both theories predict almost the same value for the exponent c ; thus at the equilibrium separation, the two values are 1.166 and 1.197, and this equality persists over a range $0 < \rho < 3$ a.u. For $\rho > 3$, the *m.o.* description breaks down, as is well known, since it predicts an equal probability of dissociation into $\text{H}^+ + \text{H}^-$ as into $\text{H} + \text{H}$. The ionic possibility is ruled out in the *e.p.* wave-function, and over this range, which is, of course, the range of Van der Waals' forces, the *e.p.* method is better. This is, however, a different problem from that of chemical binding, and provides no real argument against the *m.o.* description.

We may summarise the conclusions of this section by stating that in the simple case of H_2 , the two treatments are almost equally good; further it is agreed that in more complicated molecules, especially polar molecules, the *m.o.* treatment is superior to the *e.p.* treatment; there does, therefore, seem to be some ground for claiming that on the whole, the *m.o.* approach is somewhat more useful than the *e.p.* one. It is most unfortunate that the *m.o.* method has been systematically applied to so few molecules. The writer has applied it to a study of H_3^+ ⁹ and CH_4 ¹⁷; the work of Knipp¹⁸ on LiH^+ and James¹⁹ on Li_2^+

¹⁷ Coulson, *Trans. Faraday Soc.*, 1937, **33**, 388.

¹⁸ Knipp, *J. Chem. Physics*, 1936, **4**, 300.

¹⁹ James, *ibid.*, 1935, **3**, 9.

represent almost the only other published work effectively of this kind. Dr. W. E. Duncanson and the writer have shown, in some work shortly to be published, that the polar ion HeH^+ is another case where the *m.o.* treatment is very considerably better than the *e.p.*

One other conclusion may be drawn from this work, which has already been noticed by the writer⁹ and others, that a very considerable error will accrue if in calculating the energy, we use the naïve form of either theory, and adopt the wave-functions of the atomic orbitals without change in the molecule. An example of this error may be found in the work of Woods²⁰ on methane, where the electrons in the C atom are supposed to have the same wave-function in the molecule as in an isolated C atom. Unfortunately, we must carry through the labour of the variation of parameters if we are anxious to obtain a reliable value for the energy. And the energy curves will be uniformly flatter near their minima, in the perturbation treatment than in the variational.

5. Screening Constants for H_2 .

If we are to consider the screening effect of one electron upon the motion of the other, we are compelled to abandon the *e.p.* viewpoint, and think in terms of the *m.o.* theory, allowing each electron a separate molecular orbital, which embraces all the nuclei present in the molecule. If there were no other grounds for preference, the *m.o.* method would have considerable merit over the *e.p.* treatment, since, conceptually, it allows us to discuss the motion of the electrons separately and then allow for their interaction, whereas the pair treatment compels us to face both difficulties at once, and we lose the clarity inherent in the first picture.

The first point to make is that there are two types of screening—nuclear and electronic. Even if only one electron is present in the molecule, then, as section 3 shows, the coefficient in the exponential of the wave-function (B 2) is not the coefficient of the isolated atom. Fig. 3 shows this effect in detail; it appears that the atomic orbitals of the LCAO approximation have an effective nuclear charge about 1.2 times the real one, at the equilibrium separation. This may be called the screening due to the presence of the second nucleus; the same effect was found⁹ with H_3^+ and will hold with every molecule. At the equilibrium distance, it is probable that for non-bonding orbitals, this screening is almost negligible (*cf.* the antisymmetric orbital of H_3^+ in Fig. 3 where *c* is nearly equal to unity over the significant part of the curve) but that for bonding orbitals, the ratio of effective nuclear charge to actual nuclear charge, or, more precisely, the ratio of the exponents in the two wave-functions, is about 1.2. This ratio will increase as we compress the molecule, and decrease, to a limiting value of unity, as we stretch it.

We have yet to discuss the electronic screening. Here we meet a difficulty not found in the atomic problem. For it will appear that there are two screening constants in the molecular case; in the atomic case, the two become identical. We can illustrate this by considering the case of two electrons completing, first, the *K*-shell of an atom of nuclear charge *Z*, and second, the $\sigma 1s$ shell of a diatomic molecule, each nuclear charge being *Z*. In the atom, we use a wave-function $e^{-\sigma r}$ for each electron and find that

$$E = Pc^2 - QZc + Rc \quad \dots \quad (9)$$

²⁰ Woods, *Trans. Faraday Soc.*, 1932, 28, 877.

where P , Q and R are known constants; the term Rc is alone due to the electronic repulsions. For the molecule, just as in equation (6), we have the same expression 9, excepting that P , Q and R are now no longer constant but depend on the parameter $t = c\rho$. We do not, in this analysis, make any explicit allowance for other electrons which may be present in the atom or the molecule, but they are implicitly allowed for by the use of general rather than specific, forms for P , Q and R , and only small verbal changes are necessary to make the analysis apply equally well to such systems. Application of the variation principle to equation (9) shows that the lowest energy is obtained when

$$2Pc - QZ + R + ct \frac{dP}{dt} - tZ \frac{dQ}{dt} + t \frac{dR}{dt} = 0 \quad (10)$$

In the atomic case, the last three terms are zero; in the molecular case, they almost balance, but not quite. With the atom, this shows that the value $c = (QZ - R)/2P$ yields the best possible energy for this type of wave-function.

Now let us suppose that in the original Hamiltonian, we had omitted all the r_{12} terms and replaced Z by $Z - Z_0$. Instead of equation (9) we should have obtained the formula

$$E = Pc^2 - Qc(Z - Z_0) \quad (11)$$

The variational method gives (atomic case) for the condition of lowest energy

$$2Pc - Q(Z - Z_0) = 0.$$

This equation is identical with the true condition expressed by equation (10), if $Z_0 = R/Q$, and, correspondingly, c has the value $(QZ - R)/2P$. This is, of course, nothing but the ordinary theory of atomic screening constants.

With the molecule, the situation is more complicated because P , Q and R depend on the parameter t . Suppose, as in the atomic case, that we omitted all the r_{12} terms from the Hamiltonian and replaced Z by $Z - Z_0$, we obtain the same equation (11), though of course, P and Q vary with the nuclear separation. The variational method gives for the condition of minimum energy and most appropriate value of c

$$2Pc - QZ + ct \frac{dP}{dt} - tZ \frac{dQ}{dt} + QZ_0 + tZ_0 \frac{dQ}{dt} = 0 \quad (12)$$

This equation gives the same value of c as the full equation (10) if

$$R + t \frac{dR}{dt} = Z_0 \left(Q + t \frac{dQ}{dt} \right).$$

Calling the value of Z_0 thus obtained, Z_c , to denote that it gives the best value of c as a function of ρ , we can write

$$Z_c = \frac{R + t \frac{dR}{dt}}{Q + t \frac{dQ}{dt}} \quad (13)$$

This screening constant gives the best possible wave-function of this type of complexity, and is one of the screening constants we are seeking.

But equation (9) could equally have been written :

$$E = Pc^2 - Qc(Z - Z_e) \quad (14)$$

where

$$Z_e = R(t)/Q(t) \quad (15)$$

At first sight, it looks as though we ought to have chosen Z_e as our screening constant, rather than Z_c . But if we use the variational method on equation (14) to find the best value of c , we obtain the result

$$2Pc + c \frac{dP}{dt} - (Z - Z_e) \left(Q + t \frac{dQ}{dt} \right) = 0.$$

The value of c deduced from this equation is a wrong one, for the correct one is predicted by equation (10). We may not therefore use equations (14) and (15) to determine the wave-function, and the only value in the second screening constant Z_e is that it enables us to calculate the energy, once the wave-function is known. Putting it otherwise, equation (14) shows that the energy E is the same as that which we get by use of the usual formula $E = \int \psi^* H \psi d\tau$, applied to a certain fictitious problem; this fictitious problem is that of two non-interacting electrons, moving in the presence of nuclear charges $Z - Z_e$, and having wave-functions whose exponent c is already known by equation (12). In order to obtain the correct energy, however, we must use this value of c defined by equation (12), and not try to calculate it directly, as a variational problem, from equation (14). This makes the screening constant Z_e of less value than Z_c (although it is simpler) because the true values of c must be known before Z_e is of any use for determining the energy and this value of c depends on a prior knowledge of Z_c , which is therefore more fundamental. It should, however, be noticed that if we use the value of Z_c obtained from equation (13), to find the true value of c , we shall obtain a wrong value for the energy if we continue to use the same modified Hamiltonian (which omits the r_{12} terms and replaces Z by $Z - Z_e$). In essence the situation is that it is impossible to obtain a modified Hamiltonian by smoothing-out the electron interaction terms such that we can use this new Hamiltonian to determine at the same time both the correct energy and the correct wave-function. Z_c and Z_e are the two screening constants which do give us, under certain conditions, the best value of c , and the best value of the energy, respectively. And since it is the wave-functions that we are usually most interested in when we talk about screening constants, and since Z_e is only of value when Z_c is already known, therefore Z_c is the more important of the two.

Both Z_c and Z_e are, unfortunately, functions of t , and hence of the nuclear separation ρ . Their precise values are shown in Fig. 7, where it appears that they behave in a similar way, and that at the equilibrium separation, their values are about 0.202 and 0.178 respectively. These results are a generalisation of the atomic calculations of Eckart and others.¹ Reference to equation (13) proves, as was stated earlier, that with atoms the two screening constants are identical, for R and Q are constants and hence $Z_c = R/Q = Z_e$.

It must be borne in mind, of course, that a measure of approximation is inherent in our choice of screening constant; it is obviously inaccurate to say that the screening of the first electron upon the second is merely to change the effective nuclear charges, just as it is inaccurate to say that

in the ground state of the Helium atom, the electron repulsion is duly allowed for if we replace the central charge by $2 - 5/16$ instead of 2. In the Helium atom, the effective nuclear charge is 2 when the second electron is near the nucleus and it diminishes, as a Hartree self-consistent field shows, down to 1 when the electron is far out. The same will be true of the molecular problem, though even when the electron is close in to one nucleus, it is no longer possible to assign localised effective charges because of the diffuse charge-cloud around the other nucleus.

It would have been possible to choose other representations of the electron screening; following one method used in atomic calculations, in calculating the motion of electron 2, we might have supposed that all the charge cloud of electron 1 was distributed on a sphere of convenient radius whose centre was at the mid-point of the nuclei; or we might (more easily, if we were using spheroidal co-ordinates) have supposed that it was distributed on the surface of a suitable ellipsoid of revolution with its foci at the nuclei; another possibility would have been to suppose that it could be replaced by a uniform line charge joining the two nuclei. Each of these representations would give a different set of screening constants, and it must be emphasised that it is merely convenience of calculation (a not inconsiderable item in molecular problems) that leads us to suppose that the screening due to electron 1 could be allowed for by a suitable change of the nuclear charges. And because by no method can the screening be accurately allowed for, a certain approximation is necessarily introduced.

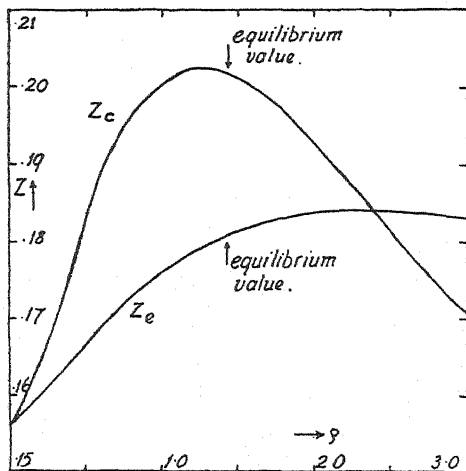


FIG 7.—Electronic screening constants.

We can summarise the results of the treatment in the case of H_2 by illustrating the method with a numerical example. Suppose it is desired to find the screening constants in the case of H_2 when $\rho = 2.0$ a.u. It is seen from Fig. 5 that this value of ρ corresponds to $c = 1.080$ approximately and thus $t = 2.160$. Using this value and the explicit forms of equations (13) and (14) (which are rather complicated), we obtain the values of Z_c and Z_e shown in Fig. 7. The correct energy corresponding to $\rho = 2.0$ a.u. is just twice that which corresponds to a single electron moving in the potential field of charges $1.00 - 0.184 (= 0.816)$ and with wave-function of type (B 2), having $c = 1.080$. Thus, so far as the energy is concerned, we can omit the electron repulsions and replace each proton by a positive charge 0.816 (but only at $\rho = 2.0$ and we must use the value of c determined from Fig. 5). On the other hand, the best wave-function is obtained if we omit the electron repulsion, and replace each proton

²¹ Dickinson, *J. Chem. Physics*, 1933, 1, 317.

²² Van Vleck, *Proc. Nat. Acad. Sci.*, 1926, 12, 662.

²³ Gordadse, *Z. Physik*, 1935, 96, 542; 1936, 99, 287.

by a charge $1.00 - 0.193 (= 0.807)$. The wave-functions thus obtained are wave-functions for two separable non-interacting electrons, but they will be the best wave-functions that we can obtain, using the orbitals (B 1) and (B 2) for the genuine H_2 molecule, when the nuclear separation is 2.0 a.u.

Note added in Proof.

The variation of the exponent c with internuclear distance has recently been discussed by Hirschfelder and Kincaid²⁴ from the point of view of the Virial Theorem. These authors show that $c (= s)$ may be regarded as a "scale factor" and the variation of c to get the lowest energy is equivalent to changing the scale so that the Kinetic Energy (T) and the Potential Energy (V) shall be related by the Virial Law $T = -V/2$. In particular, although they do not calculate the correct value, these authors (p. 661) show why the Wang value for the fundamental vibration frequency of H_2 is too high; a consideration of Fig. 1 of their paper shows that the energy plotted in contours as a function of c and ρ varies very much more rapidly along the line $c = 1.166$, than along the curve of best values of c . It is not difficult from their curve to believe that the difference thus obtained is as great as the present writer's calculation in section 4 makes it out to be.

Summary.

A critical comparison is given of the molecular orbital and electron-pair treatments of the ground state of the Hydrogen molecule, and it is shown that the two theories are almost equally valid. Several errors in the results of other workers are corrected, and the extreme sensitiveness of the fundamental frequency to small changes in the wave-function, is examined. It is shown that in molecular problems, there are two kinds of screening constant, nuclear and electronic; both types are discussed in some detail and their variation with internuclear separation is investigated fully.

²⁴ Hirschfelder and Kincaid, *Physic. Rev.*, 1937, **52**, 658.

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THE PLATINUM ELECTRODE AS A CATALYST FOR THE ACTIVATION OF HYDROGEN II.

BY M. CALVIN AND H. E. DYAS.

Received 27th July, 1937.

In a previous communication¹ M. Calvin described the effects of polarisation on the catalytic power of platinised platinum on the atomic exchange reaction between hydrogen and water. An important point in that description was based only on a qualitative statement of one observation. It is the object of this note to amplify that statement by experimental data which have since confirmed it.

The statement to which we refer was this: cathodic polarisation of the order of 0.01 volts causes a considerable reduction of the rate of

¹ M. Calvin, *Trans. Faraday Soc.*, 1936, **32**, 1428.

catalytic interchange between hydrogen and water while at the same time the catalytic *para*-hydrogen conversion which on the unpolarised catalyst proceeds at the same rate of the exchange reaction persists and is, indeed, more rapid than it is on the unpolarised catalyst. In the new experiments we have used the $\text{H}_2 + \text{D}_2 = 2\text{HD}$ reaction instead of the *para*-hydrogen conversion.

We again observed that the interchange between hydrogen and water was slowed down considerably by cathodic polarisation. As to the $\text{H}_2 + \text{D}_2$ reaction, we found that it does not proceed at all on the unpolarised catalyst while it makes its appearance when polarisation is applied. The rate of this reaction can, in fact, be higher than the rate of the hydrogen-water exchange on the unpolarised catalyst. The attached table shows the experimental results, including those which were discussed but not stated in the previous paper.

Experimental.

The apparatus was essentially the same as that previously described, except that the calomel electrode was now attached directly to the reaction vessel as part of the vacuum system. A plug of glass wool and agar gell was inserted in the connecting tube to minimise diffusion of the calomel cell electrolyte into the reaction vessel. Thus the necessity for reducing the pressure in the calomel cell independently of the rest of the system was eliminated.

The gas was analysed by the high pressure thermal conductivity method of Bonhoeffer and Harteck.² The resistance shift for gas containing 55 per cent. D_2 was about 3.5 ohms and when equilibrated on a hot tungsten wire so that the equilibrium mixture of H_2 , HD and D_2 was obtained the shift was about 2.5 ohms. This shift of 1.0 ohms due to equilibration according to the reaction $\text{H}_2 + \text{D}_2 = 2\text{HD}$ was the same over the range of deuterium content from 45 to 55 per cent. We were thus able to determine both the total D content and the degree of equilibration to HD in a single sample of gas, when the total D content did not drop too far.

Procedure.

For each run a new charge of gas was admitted into the reaction system and at the end of the run it was dried by passage through a liquid air trap and collected in a bulb which could be transferred to the analysis apparatus. The thermal conductivity was measured and then the gas was run into an equilibration vessel containing a tungsten filament which could be heated to 1000° or more. After equilibration the thermal conductivity was again measured. The difference in these two resistance readings compared to the original HD shift of about 1 ohm would then give a measure of the amount of HD appearing in the gas. By adding the 1 ohm to the resistance value for the equilibrated mixture the HD shift was eliminated and the resulting resistance value corresponded to the total D content as D_2 .

Result.

A set of typical results are presented in the Table. All the data contained therein was taken at room temperature (18°) and in 1 N H_2SO_4 . Catalysts 1, 2 and 3 represent three independent platinisations of the electrode. $\Delta\phi$ is the cathodic overpotential applied to the plate, *i.e.* the potential on the plate in excess of what it would normally assume in the particular solution at the given gas pressure (P_{H_2}), i is the current required to maintain this overpotential, t is the time of the run and $k_{(\text{ex})}$ and $k_{(\text{HD})}$

² Bonhoeffer and Harteck, *Z. physik. Chem.*, B, 1929, 4, 113.

are the first order velocity constants of the exchange and of the HD reactions respectively. The variation of k to be expected from the small variations in P_{H_2} are within the experimental error of k .

TABLE.—TEMPERATURE 18°.*

Catalyst.	Potential-Volt $\Delta\phi$.	i (mils).	Time (hours).	$k_{(ex)}$.	$k_{(HD)}$.	P_{H_2} .
1.	·007	·42	21·8	·00085	·0126	90 mm.
	0	0	21	·0042	~0	100 "
2.	0	0	24·1	·0055	~0	135 "
	·003	·2	23	·0009	·0034	160 "
3.	0	0	23·2	·023	~0	95 "
	·0008	·1	20·2	·016	~0	85 "
4.†	0	0	25	·007	·026†	382 "
	·005	—	24	·002	·085†	382 "

* *Para*-conversion is generally about 3 times faster than $H_2 + D_2$ reaction. Thus 3 k_{HD} would give the probable value for *para*-conversion under same circumstances.

† No. 4 is the result which was mentioned in the previous paper, the numerical value of which was, however, not there given. The constants given in the $k_{(HD)}$ column are, in this case, for the *para*-conversion.

Discussion.

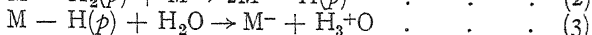
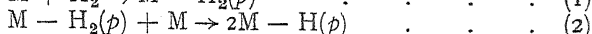
It was said before that the changes caused by cathodic polarisation confirm the views of Hammett³ on the nature of overvoltage on platinised platinum. We wish to add here some more details to this point.

Hammett derives from an analysis of current voltage curves that for small cathodic overvoltages the rate determining factor is the recombination of the adsorbed atoms deposited by the electrolysis, whereas for higher overvoltages in the region of 0·01 volt the discharge of the ions becomes rate determining. This would require that at low overvoltage practically every H_2 molecule dissociating will form H ions and hence no HD will appear in the gas. On the other hand, on cathodically polarised electrodes the atoms formed by dissociation of hydrogen would mainly return to the molecular state without exchanging with water. The *para*-hydrogen conversion observed on the unpolarised plate is due to the exchange reaction.

Our observations confirm these conclusions but they contain an element which is not included in them. We find that the dissociation of H_2 molecules can be made to proceed more rapidly on the cathodically polarised electrode than on the unpolarised one. Also in the previous paper it was reported that when the exchange due to simple electrolysis was taken into account anodic polarisation actually reduced the catalytic exchange. It seems difficult to account quantitatively for these observations but it appears worth while to consider a framework into which they can be fitted.

If we add to the mechanism proposed by Hammett, the condition that both the molecularly and the atomically adsorbed hydrogen are polar it becomes possible at least qualitatively to account for all of the observations. The complete process can be represented by :

³ Hammett, *Trans. Faraday Soc.*, 1933, 29, 770.



The subscript (*p*) indicates that the structure contains a dipole but the orientation of this dipole is not specified. This is also in agreement with the data of Farkas ⁴ and Eley and Polanyi ⁵ who have shown that on unpolarised platinum the *para-ortho* conversion never goes faster than 2-3 times the rate of exchange, although both rates are influenced by the acidity of the solution since both the initial and final states of the rate determining reaction (3) are polar.*

When the electrode is polarised cathodically reaction (3) is inhibited and at the same time reaction (2) is accelerated. Thus cathodic polarisation can inhibit the exchange reaction which must pass through (3) and accelerate the $H_2 + D_2 = 2HD$ reaction which requires only (2). Also at very low overvoltages the deposition of hydrogen will be limited by (2) and as the potential is increased the rate of (2) will increase until it becomes greater than that of (3) at which point (3) will dominate in controlling the rate of hydrogen evolution.

On the other hand, when the electrode is polarised anodically the reverse effects should take place, *i.e.* (3) should be accelerated and (2) decelerated. But since (2) is already the slower of the two, the overall effect on the exchange will be one of retardation, but not so great an effect as the retardation of (3) by cathodic polarisation, since in that case ions are concerned whereas in this case only dipoles are concerned. This has, in fact, already been indicated by experiments.

The authors wish to express their great indebtedness to Professor M. Polanyi for suggesting these experiments, for many discussions and his constant interest in this work, and for the opportunity to work in these laboratories.

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The University of Manchester.*

⁴ Farkas and Farkas, *Trans. Faraday Soc.*, 1937, **33**, 678.

⁵ Eley and Polanyi, *ibid.*, 1936, **32**, 1388.

* Farkas tends to disagree with this.

THE NEAR ULTRAVIOLET ABSORPTION SPECTRUM OF ACETONE VAPOUR.

BY W. ALBERT NOYES, JR.

Received 29th September, 1937.

The ultraviolet absorption spectrum of acetone has been investigated ^{1, 2} as far as 800 Å. In the near ultraviolet acetone absorbs in the same general region as do all other aldehydes and ketones. On the long wave side of what seems (superficially at least) to be a region of continuous absorption, weak bands have been observed by several investigators. The long wave edges of several of these bands were measured

¹ Noyes, Duncan and Manning, *J. Chem. Physics*, 1934, **2**, 717.

² Duncan, A. B. F., *J. Chem. Physics*, 1935, **3**, 131.

and an empirical scheme presented which accounted for most of the bands.¹ In this scheme one ground state frequency of approximately 370 cm^{-1} (with $\nu'' = 0, 1, 2$) and two upper state frequencies of approximately 210 and 1200 cm^{-1} were employed. Since the changes in relative intensities of the bands with temperature were not investigated the scheme could be considered only as an empirical method of fitting the bands together.

In any molecule as complex as acetone many different modes of vibration are possible so that the vibration analysis of an electronic band system becomes difficult. It is probably true that no such analysis which would be entirely free from criticism has been presented except for a few simple molecules where, for special reasons, one upper state frequency alone seems to be excited. While the general principles governing such transitions are now understood, many details of the application of the theory have not been and probably will not be in the near future worked out. By comparing spectra of molecules which are related in their structures and properties important information may be obtained, but a detailed analysis of a band system must, at the present time, be presented with proper reservations.

If the methyl groups in acetone are considered as points, this molecule would belong to the same symmetry group as formaldehyde (C_{2v}). However the rotation of the methyl groups around the carbon-carbon bonds will upset this symmetry and the extent to which this will modify the selection rules is at present unknown. The best one can say at present is that those vibrations which are totally symmetrical under the transformations of group C_{2v} will probably be excited with greatest probability by electron transition in acetone.

In the present investigation the near ultraviolet absorption spectrum has been photographed in a one meter tube at fairly low pressure and at two temperatures: approximately 20° C. and 200° C. Microphotometer records have been made and an attempt made to find some of the important features which would constitute the beginning of a vibration analysis of this band system. A Hilger E_2 spectrograph was used.

Description of the Spectra.

An examination of the spectra taken at various pressures and temperatures reveals at once that under otherwise identical experimental conditions the apparent 'continuum' extends to longer wave-lengths at high temperatures than at low and that to the naked eye as well as under low power magnification the 'bands' are scarcely visible at all at 200° C. regardless of pressure. The microphotometer record reveals that this is probably due rather to the superposition of a lot of structure than to its absence. Whether this is true at room temperature in the region when the absorption is apparently continuous is an open question.

The microphotometer records show that structure is observed at longer wave-lengths at high temperatures than at low. This is, of course, to be expected if the effect of higher vibration levels of the ground state is taken into account. However the general absorption is so much greater at 200° than at room temperature that it is very difficult to compare intensities of a given band at two different temperatures except, perhaps, near the long wave limit of the absorption region.

The wave-lengths of a large number of bands have been determined in the present investigation both with the microscope and from the microphotometer records. In all cases the frequencies agree within the previously assigned limits ($10\text{--}15\text{ cm}^{-1}$) with the values previously reported.

However, it is evident from the microphotometer records that each 'band' consists in reality of a series of subsidiary maxima, the exact number to be associated with a given 'band' being difficult to decide upon. In this respect the near ultraviolet bands resemble² those between 1960 and 1820 Å. The frequency range in a given 'band' may be considerable.

The difficulty in seeing the bands either with the naked eye or under low-power magnification is further borne out by the microphotometer records. The contrast between the bands and the surrounding absorption is in all cases small. It becomes meaningless to try to decide, in a case such as this, whether the appearance of a band does or does not imply predissociation.

Prominent Frequency Differences.

The same prominent differences in frequency are observed in the present work as have been reported, except that the difference of 210 cm^{-1} should probably not be taken as a vibration frequency of the upper state. The progressions beginning with 30839 and 30925 cm^{-1} are probably based on subsidiary maxima. The assignment of a definite frequency to either the upper or lower states involves taking differences between the proper sub-maxima (long wave edges were used as previously). In the absence of a theoretical explanation of these maxima, this cannot be done unambiguously. Table I illustrates the difficulties involved.

TABLE I.—FREQUENCY DIFFERENCES BETWEEN MAXIMA.

30941	(21)	30920	(30)	30890	(51)	30839	(44)	30795
365		364		364		368		365
31306	(22)	31284	(30)	31254	(47)	31207	(47)	31160

In some cases the lateral displacement of a row will still reveal differences in frequency similar to those found in Table I, so that it is impossible to identify the true vibration frequencies with certainty at present.

It is quite evident upon inspection of the plates and the microphotometer records that the frequency of 360-370 cm^{-1} belongs to the upper and not to the lower state. Table II shows a series of bands which probably form a progression, although the differences between the higher members are less certain than those at the beginning due to the large amount of structure which is present.

The low frequencies found in the Raman spectrum of acetone³ are 391, 486, 532, 594, 787. The Boltzmann factors for these are such that they would be appreciably excited at 200° C. Here again the positive identification of the ground state frequencies is not possible, but on the basis of comparative intensities at 25° C. and 200° C., the classification of certain bands as coming from higher levels in the ground state is rendered reasonable. Table III shows a few frequency differences obtained in this manner.

TABLE II.—PROBABLE PROGRESSIONS IN ACETONE.

30890	(51)	39830
372		368
31262	(55)	31207
365		361
31627	(59)	31568
344		353
31971	(50)	31921
341		340
32312	(51)	32261
		329
		32590
		311
		32901

² Kohlrausch and Köppl, *Z. physik. Chem.*, B, 1934, 24, 385.

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Bands are observed as far as 30189 at 200° so that still other frequencies in the ground state should be used in a complete analysis.

Also a frequency of about 1200 cm^{-1} in the upper state was found before (probably a carbon oxygen frequency). Table IV shows differences which made this frequency quite plausible.

TABLE III.—PROBABLE GROUND STATE DIFFERENCES IN ACETONE.

30890	(395)	30495	(477)	30413
31262	(400)	30862	(482)	30780
31627	(383)	31244	(476)	31151
31971	(403)	31568	(487)	31484
32312	(396)	31916	(493)	31819
Av.	(394)	Av.	(483)	

A more detailed classification of the bands would be largely meaningless for a spectrum as

complex as the one under consideration, although empirically it would be possible to account for all or nearly all of the bands in detail.

TABLE IV.—UPPER STATE FREQUENCY DIFFERENCE OF ABOUT 1200 cm^{-1} .

30941	30920	30890	30839	30795
1212	1211	1203	1206	1212
32153	32131	32093	32045	32007

Conclusions.

The near ultraviolet bands of acetone cannot be classified completely by other than empirical methods. However the general characteristics of the spectrum make it appear very probable that frequencies of about 370 and 1205 cm^{-1} are characteristic of the upper state. Comparison of absorption spectra taken at room temperature and at 200° C. shows certain bands to come definitely from higher levels of the ground state. Important differences of 394 and 483 cm^{-1} probably should be correlated with Raman lines in acetone, but the identification of these frequencies is not certain due to the large amount of structure which is observed, particularly at the higher temperature.

The author wishes to express his appreciation to Professor R. G. W. Norrish, F.R.S., for extending the facilities of the Laboratory of Physical Chemistry at Cambridge, where this work was carried out. His thanks are due also to Professor Stratton, D.S.O., and the staff of the Solar Physics Laboratory for preparing the microphotometer tracings.

THE VALENCE-BOND TREATMENT OF THE OXYGEN MOLECULE.

BY G. W. WHELAND.¹

Communicated by PROFESSOR J. E. LENNARD-JONES.

Received 30th August, 1937.

As is well known,² the molecular orbital method predicts unambiguously that the normal oxygen molecule should be in a ${}^3\Sigma_g^-$ state. This prediction is confirmed by experiment. The valence-bond method, on the other hand, apparently predicts a singlet instead of a triplet ground state, since the full stabilising effect of a double bond can be obtained only if each electron is paired against another with opposed spin. This has frequently been brought forward as a case in which the valence-bond method fails even qualitatively to provide the correct answer. The explanation of the difficulty, however, soon becomes apparent if the problem is examined more closely.³

For simplicity, we shall neglect the $2s$ electrons as well as those of the K shells. The atomic orbitals to be considered are therefore the $2p$ functions, p_0 , p_+ , and p_- , for one atom and p'_0 , p'_+ and p'_- for the other. If the two nuclei are taken to lie on the z -axis, then p_0 and p'_0 overlap strongly and can be considered bonded together. It will involve no serious loss of generality if, in the following discussion, we regard these two orbitals as constituting a single bond and ignore their interaction with the remaining electrons. The problem, accordingly, reduces to one of six electrons, which are to be assigned, with suitable spins, to the four orbitals, p_+ , p_- , p'_+ , p'_- . This can be done in the sixteen different ways shown in Table I, where as usual, the m_s refers to the component of electron spin and m_l to the component of orbital momentum. (The assignments for which $\Sigma m_s \neq 0$ add nothing new and have been omitted.) Of these, the first eight correspond to the formation of a purely covalent molecule from electrically neutral atoms, while the last eight correspond to the formation of an ionic molecule from O^+ and O^- ions. For the moment, we shall consider only the first group, since this is doubtless the more important.

The functions, Ψ_I and Ψ_{II} , which are represented by the first two rows of the table, have $\Sigma m_l = 2$ and therefore cannot combine with any of the others, $\Psi_{III} \dots \Psi_{VIII}$. They lead to a ${}^1\Delta_g$ function,

¹ Foreign Fellow of the John Simon Guggenheim Memorial Foundation, 1936-37.

² J. E. Lennard-Jones, *Trans. Faraday Soc.*, 1929, **25**, 668.

³ The following discussion resembles but is not completely equivalent to the discussions of the same problem by W. Heitler and G. Pöschl, *Nature*, 1934, **133**, 833, and by G. Nordheim-Pöschl, *Ann. Physik*, 1936, **26**, 258. Their treatments were based upon the method of spin-valence, which considers the interaction between entire atoms in definite spectroscopic states and not those between uncoupled atomic orbitals.

TABLE I.

	p_+	p_-	p'_+	p'_-	Σm_s	Σm_l	States.
I	$+-$	$+$	$+-$	$-$	0	2	${}^1\Delta_g, {}^3\Delta_u$
II	$+-$	$-$	$+-$	$+$	0	2	
III	$+-$	$+$	$-$	$+-$	0	0	
IV	$+-$	$-$	$+$	$+-$	0	0	${}^1\Sigma_g^+, {}^1\Sigma_u^-, {}^3\Sigma_g^-, {}^3\Sigma_u^+$
V	$+$	$+-$	$+-$	$-$	0	0	
VI	$-$	$+-$	$+-$	$+$	0	0	
VII	$+$	$+-$	$-$	$+-$	0	-2	${}^1\Delta_g, {}^3\Delta_u$
VIII	$-$	$+-$	$+$	$+-$	0	-2	
IX	$+-$	$+-$	$+-$	$-$	0	2	
X	$+-$	$-$	$+-$	$+-$	0	2	${}^1\Delta_g, {}^1\Delta_u$
XI	$+-$	$+-$	$+$	$-$	0	0	
XII	$+-$	$+-$	$-$	$+$	0	0	
XIII	$+$	$-$	$+-$	$+-$	0	0	${}^1\Sigma_g^+, {}^1\Sigma_u^+, {}^3\Sigma_g^-, {}^3\Sigma_u^-$
XIV	$-$	$+$	$+-$	$+-$	0	0	
XV	$+-$	$+-$	$+-$	$+-$	0	-2	
XVI		$+-$	$+-$	$+-$	0	-2	${}^1\Delta_g, {}^1\Delta_u$

Each of the rows, I . . . XVI, corresponds to a function, $\Psi_I \dots \Psi_{XVI}$, obtained by assigning electrons with positive or negative spin to the various orbitals as indicated by the $+$ and $-$ signs. In Ψ_I , for example, electrons with positive spin are assigned to p_+ , p_- , and p'_+ , and with negative spin to p_+ , p'_+ , and p'_- .

$\frac{1}{2^{\frac{1}{2}}}(\Psi_I \cdot \Psi_{II})$, and a ${}^3\Delta_u$ function, $\frac{1}{\sqrt{2}}(\Psi_I + \Psi_{II})$, with energies

$$W({}^1\Delta_g) = Q - 2(p_+p_-) - 2(p_+p'_-) - (p_+p'_+)$$

and

$$W({}^3\Delta_u) = Q - 2(p_+p_-) - 2(p_+p'_-) - 3(p_+p'_+).$$

Q is the coulomb integral, $(p_+p_+p_-p'_+p'_+p'_- | H | p_+p_+p_-p'_+p'_+p'_-)$; (p_+p_-) is the single exchange integral between p_+ and p_-

$$(p_+p_+p_-p'_+p'_+p'_- | H | p_+p_-p_+p'_+p'_+p'_-);$$

and similarly for $(p_+p'_-)$ and $(p_+p'_+)$. The higher exchange integrals of the energy and all exchange integrals of unity have been neglected. In the derivation of the above expressions, use has been made of the equalities, $(p_+p_-) = (p'_+p'_-)$, $(p_+p'_-) = (p_-p'_+)$, and $(p_+p'_+) = (p_-p'_-)$, which follow from considerations of symmetry. Since the orbitals p_+ and p'_+ are not orthogonal to each other, their exchange integral $(p_+p'_+)$ is presumably negative, so that the ${}^1\Delta_g$ state lies lower than the ${}^3\Delta_u$.

The functions, Ψ_{VII} and Ψ_{VIII} , combine in a similar way to give a ${}^1\Delta_g$ and a ${}^3\Delta_u$ state with $\Sigma m_l = -2$. These new states, of course, have exactly the same energies as the two above, and in fact, they represent merely the second components of the doubly degenerate Δ levels.

Now let us consider the functions, $\Psi_{III} \dots \Psi_{VI}$, which correspond to Σ levels⁴ with $\Sigma m_l = 0$. First, Ψ_{III} and Ψ_{IV} can be combined to give a singlet, $\frac{1}{\sqrt{2}}(\Psi_{III} \cdot \Psi_{IV})$, and a triplet, $\frac{1}{\sqrt{2}}(\Psi_{III} + \Psi_{IV})$, with energies

$$W({}^1\Sigma) = Q - 2(p_+p_-) - (p_+p'_-) - 2(p_+p'_+)$$

and

$$W({}^3\Sigma) = Q - 2(p_+p_-) - 3(p_+p'_-) - 2(p_+p'_+).$$

⁴ The two different uses of the symbol Σ must not be confused here.

The integrals, Q , (p_+p_-) , etc., can be shown to have the same values as in the previous cases. The triplet lies lower than the singlet, since the orbitals, p_+ and p'_- , are orthogonal and their exchange integral $(p_+p'_-)$, is therefore necessarily positive. If now we compare this triplet with the ${}^1\Delta_g$ previously considered, we find that the latter is probably the more stable. In fact,

$$\begin{aligned} W({}^3\Sigma) - W({}^1\Delta_g) &= - (p_+p'_-) - (p_+p'_+) \\ &= - (p_xp'_y) - (p_xp'_x). \end{aligned}$$

The functions, p_x and p_y , employed in the last row, are the real $2p$ orbitals projecting along the x and y axes respectively, so that $(p_xp'_y)$ and $(p_xp'_x)$ are simply the negatives of the integrals, $C_{\pi\pi'\pi\pi}$ and $C_{\pi\pi\pi\pi}$, respectively, used by Penney.⁵ The first of these is positive and probably comparatively small, while the second is negative and probably somewhat larger in magnitude. $W({}^3\Sigma) - W({}^1\Delta_g)$, accordingly, is positive and perhaps of the order⁶ of 1 e.v.

In exactly the same way, the functions Ψ_V and Ψ_{VI} , combine to form a singlet, $\frac{1}{\sqrt{2}}(\Psi_V - \Psi_{VI})$, and a triplet, $\frac{1}{\sqrt{2}}(\Psi_V + \Psi_{VI})$, which have the same energies as the above. None of these four functions, however, can represent actual states of the molecule, since none satisfy the necessary symmetry conditions. Instead, the two singlets must be combined with each other, and the two triplets likewise. Thus we obtain

$$\begin{aligned} {}^1\Sigma_g^+ &: \frac{1}{2}(\Psi_{III} - \Psi_{IV} + \Psi_V - \Psi_{VI}) \\ {}^1\Sigma_u^- &: \frac{1}{2}(\Psi_{III} - \Psi_{IV} - \Psi_V + \Psi_{VI}) \\ {}^3\Sigma_g^- &: \frac{1}{2}(\Psi_{III} + \Psi_{IV} - \Psi_V - \Psi_{VI}) \\ {}^3\Sigma_u^+ &: \frac{1}{2}(\Psi_{III} + \Psi_{IV} + \Psi_V + \Psi_{VI}). \end{aligned}$$

The energies are now different from those given above for the uncombined ${}^1\Sigma$ and ${}^3\Sigma$ levels. In particular, one triplet, the ${}^3\Sigma_g^-$, has become more stable, and the other, the ${}^3\Sigma_u^+$, has become less stable by an equal amount.

$W({}^3\Sigma_g^-) = Q - 2(p_+p_-) - 3(p_+p'_-) - 2(p_+p'_+) - \frac{1}{2}(\Psi_{III} + \Psi_{IV} | H | \Psi_V + \Psi_{VI})$
and

$W({}^3\Sigma_u^+) = Q - 2(p_+p_-) - 3(p_+p'_-) - 2(p_+p'_+) + \frac{1}{2}(\Psi_{III} + \Psi_{IV} | H | \Psi_V + \Psi_{VI})$

(The two ${}^1\Sigma$ states as a group are less stable than these and need not be considered further.) If Herzberg's value is accepted for the ${}^3\Sigma_g^- - {}^3\Sigma_u^+$ separation, we deduce that

$$(\Psi_{III} + \Psi_{IV} | H | \Psi_V + \Psi_{VI}) = 4.7 \text{ e.v.}$$

⁵ W. G. Penney, *Proc. Roy. Soc., A*, 1934, 144, 166.

⁶ It would make no great difference in the following argument if this estimate were in error by as much as ± 100 per cent. L. Pauling and G. W. Wheland, *J. Chem. Physics*, 1933, 1, 362, found that for the carbon-carbon integral analogous to $(p_xp'_x)$ they had to assume a value of about -1.5 e.v. in order to obtain agreement between the calculated and observed resonance energies. On the other hand, W. G. Penney⁵ found that $(p_xp'_x) - (p_xp'_y)$ had to be equal to -0.72 e.v. in the carbon-carbon case in order to account for the torsional frequency of ethylene. These two results are mutually inconsistent, since $(p_xp'_y)$ is necessarily positive, but they agree sufficiently well as regards order of magnitude to suggest that the permissible limit of error may not be exceeded. We shall see below that the spectroscopic data for O_2 require that $-(p_xp'_x) - (p_xp'_y)$ be actually a little smaller than 1.4 e.v.

consequently

$$\begin{aligned} W(^3\Sigma_g^-) - W(^1\Delta_g) &= -(\phi_x\phi'_y) - (\phi_x\phi'_x) - \frac{1}{2}(\Psi_{\text{III}} + \Psi_{\text{IV}} | H | \Psi_{\text{V}} + \Psi_{\text{VI}}) \\ &= -(\phi_x\phi'_y) - (\phi_x\phi'_x) - 2.35 \text{ e.v.} \end{aligned}$$

The $^3\Sigma_g^-$ level is therefore more stable than the $^1\Delta_g$, unless

$$-(\phi_x\phi'_y) - (\phi_x\phi'_x)$$

has an improbably large value in excess of 2.35 e.v. It is known experimentally that

$$W(^3\Sigma_g^-) - W(^1\Delta_g) = -0.97 \text{ e.v.}$$

so that complete agreement can be obtained by setting

$$-(\phi_x\phi'_y) - (\phi_x\phi'_x) = 1.38 \text{ e.v.}$$

This value is quite reasonable, although it may seem rather high.

The above discussion shows that the valence-bond treatment can account reasonably well for the observed spectroscopic state of the normal oxygen molecule when it takes into account the covalent functions, $\Psi_{\text{I}} \dots \Psi_{\text{VIII}}$. It is now necessary to show that the inclusion of ionic terms involving the functions, $\Psi_{\text{IX}} \dots \Psi_{\text{XVI}}$, is not apt to alter the situation. First, we note that $\frac{1}{\sqrt{2}}(\Psi_{\text{IX}} + \Psi_{\text{X}})$ gives a $^1\Delta_g$ function with $\Sigma m_l = 2$, which can combine with and stabilise further the $^1\Delta_g$ state formed from Ψ_{I} and Ψ_{II} . [In the same way, $\frac{1}{\sqrt{2}}(\Psi_{\text{XV}} + \Psi_{\text{XVI}})$ gives the other component of this $^1\Delta_g$ level and combines with the one formed from Ψ_{VII} and Ψ_{VIII} .] This effect, however, is counter-balanced by the fact that $\frac{1}{2}(\Psi_{\text{XI}} + \Psi_{\text{XII}} + \Psi_{\text{XIII}} + \Psi_{\text{XIV}})$ gives a $^3\Sigma_g^-$ function, which similarly combines with and stabilises the ground state of the molecule. Moreover, the last of these new ionic functions can be shown to correspond to a lower energy than the first two, so that the relative order of stability should not be altered from that found previously.

In conclusion, it should be noted that the ionic functions, $\Psi_{\text{XI}} \dots \Psi_{\text{XIV}}$, do not give rise to a $^3\Sigma_u^+$ state. Consequently the observed $^3\Sigma_g^- - ^3\Sigma_u^+$ separation of 4.7 e.v. must be somewhat larger than the integral $(\Psi_{\text{III}} + \Psi_{\text{IV}} | H | \Psi_{\text{V}} + \Psi_{\text{VI}})$. This has the result of lowering the calculated value of $-(\phi_x\phi'_y) - (\phi_x\phi'_x)$ by perhaps a few tenths of an electron volt below the former figure of 1.38 e.v.

The author wishes to express his appreciation to Professor Lennard-Jones for his assistance and encouragement in the preparation of this paper.

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Cambridge.*

² H. Sponer, *Molekülspektren* (Springer, Berlin, 1936).

ERRATUM.

Page 1363, line 6 from bottom:—

For OMoO_4 and OMoF_8 , respectively, read: OsO_4 and OsF_8 .

REVIEWS OF BOOKS.

- A Commentary on the Scientific Writings of J. Willard Gibbs.
Volume I: Thermodynamics, pp. xxiii and 742. Volume II:
Theoretical Physics, pp. xx and 605. Oxford: The University
Press. Price 45s. each volume.

The work of J. Willard Gibbs represents one of the classical applications of mathematical analysis to the understanding of nature. Gibbs' treatment is subtle and brilliant, rigid in logic and very general in form. These admirable qualities have entailed the unavoidable difficulty of a certain inaccessibility to those for whom mathematical physics is not an end in itself, and it can safely be said that many chemists and physicists must often have used results and principles derived ultimately from Gibbs' work without ever having drunk at the fountain itself.

The idea of the two volumes of the Commentary is to dissect and explain Gibbs' methods, to elucidate, where necessary, passages presenting mathematical difficulty, and by illustration of the way in which the general and abstract treatment is applicable to specific problems of modern interest to reveal its power and increase its utility.

Volume I deals with the thermodynamical writings of Gibbs' and has been edited by Professor F. G. Donnan with an admirably chosen group of collaborators, ten in all. Volume II deals with the whole of Gibbs' work on Theoretical Physics, and is written by a distinguished group of four, under the editorship of Professor A. Haas of Vienna. Together, the volumes form an indispensable companion to the "Collected Works."

The student will want to know whether the commentary really makes things easier for him. In partial answer to this one may quote the introductory mathematical notes of Professor J. Rice, which are useful and might perhaps with advantage be more extensive: and one may explain that in Vol. I Dr. Butler, for example, goes through Gibbs' General "Thermodynamics System" almost page by page, virtually paraphrasing, as well as elucidating, much of the original text. One has the impression that the style of the commentator is didactically simpler and more concrete, and, at the very least, it can be said that any student will benefit from the stereoscopic view of the matter which he will obtain from a comparative reading of text and commentary. Likewise, changes in the order of development are of assistance, parts of Gibbs' text widely separated in the original being brought together in a manner which reveals more important organic unities. Dr. Guggenheim deals equally fully with Osmotic and Membrane Equilibria, pointing out carefully at each stage what are the essential features and the advantages of the Gibbs method. Dr. Morey deals with the Phase Rule, and includes an account of some practical applications. Professor Milne contributes a section on thermodynamic functions, and Professor Schreinemaker one on Graphical Representation. Professor Keyes deals with Ideal Gases and Gas Mixtures, Professor J. Rice with Strained Elastic Solids and with Surfaces of Discontinuity, the latter section containing a discussion of the famous Adsorption Isotherm together with other adsorption, equations in a way which brings out clearly the relation of Gibbs' work to that of later workers.

There are interesting short sections by Professor Andrews on the Equilibrium of Heterogeneous Systems under Gravity, and by Professor Harned on the applications of thermodynamic methods to electrochemistry. Professor Wilson's account of Gibbs' lectures will appeal to those interested in the problem of how to arrange for the presentation of difficult subjects to students.

The second volume is concerned principally with statistical mechanics and its relation to thermodynamics. In the various sections by Professors Haas, Epstein, Page and Wilson, practically the whole of this field is covered in a comprehensive manner. As with the first volume, much of the treatment is based upon the actual text of Gibbs but, on the whole, the method is a little more general, especially in the valuable introductory essay by Professor Haas himself and again in Professor Epstein's treatment of Modern Problems of Thermodynamics. There are, for example, discussions of wave mechanical methods, of degenerate statistics and of Nernst's theorem. Nobody would suggest, however, that the presence of these discussions of modern topics detracts from the value of the work. The sections, for example, on the relation of classical to quantum statistics will be most helpful to all students of these subjects. While the treatment of statistical physics is the most valuable part of volume II, mention should also be made of sections on light (which however is only fragmentary) and on vector analysis and multiple algebra.

Quite apart from fulfilling its function of providing a memorial to the great achievements of Gibbs the two volumes of the Commentary will not only elucidate much of his work, but also provide a storehouse of information on many matters connected with modern statistical physics and thermodynamics.

Electrical Measurements. By HARVEY L. CURTIS. London: McGraw-Hill Publishing Co. Ltd., 1937. Pp. xiv + 302. Price 24s. net.

All who are interested in exact electrical measurements, whether of this generation or of that which was nourished on a study of Gray's *Absolute Measurements* and of Rosa's remarkable papers, recognise the need for a treatise which shall combine the virtues of Gray with a recognition of the important advances made in recent years.

Dr. Curtis, in his critical study of these advances, has not forgotten to retain what is best and most noteworthy in the older work, and the story of the battle of the standards has seldom, if ever, been more fascinatingly told.

It would have been easy to overload such a work with a mass of fine detail and to have produced a ponderous *Handbuch* whose interest would be inversely as its mass. Dr. Curtis has resisted this temptation, and has withal produced an account of absolute and comparative measurements of resistance, current, inductance and capacitance which is a model of clarity and a testimonial to the author's capacity for picking out relevant and ignoring irrelevant detail.

The book is moderate in size, and not too high in price. It is admirably produced, as becomes a work which is likely to take its place as a classic treatise on the subject.

A. F.

Gases and Metals. By COLIN J. SMITHELLS. London: Chapman and Hall, 1937. Pp. vi + 218. Price 18s. net.

Equilibria between gases and metals involve three different types of phenomena: adsorption at surfaces, diffusion along intercrystalline boundaries and through metal lattices, and solubility in liquid and solid metals. These phenomena are important in such diverse industries as the metallurgical industries, the manufacture of vacuum devices, and in many important catalytic industries of modern times. From the scientific standpoint also, the study of metal-gas systems has its own intrinsic interest.

Dr. Smithells has attempted to collect the available scientific data in these several fields in the present volume and to show the interconnection between varied methods of approach to the equilibria in question. Experimental methods are outlined and detailed discussions are given of fundamental principles and theory. Among recent work thus discussed may be noted activated adsorption, chemisorption, and the data of Roberts with gases on clean tungsten surfaces. Surface migration of adsorbed gases, activated diffusion along cracks and through lattices, the effect of impurities on adsorption and diffusion and of lattice imperfections are also given detailed treatment. In the section on solution the reviewer was surprised at the wide range of gases and metals for which data are available. The volume should be a welcome addition to the literature of the subject, valuable both for its method of presentation and as a collection of the available literature. It is well printed, with nearly 150 legible diagrams. Only minor errors have been noted. The reviewer would himself prefer a less bulky volume on more flexible paper.

HUGH S. TAYLOR.

Electren Tubes in Industry. By KEITH HENNY. McGraw Hill Publishing Co., Ltd. Pp. viii + 539. Price 30s. net.

This book by the editor of *Electronics* has for its purpose to acquaint industrial engineers, teachers, and students with the many applications of electron tubes to non-communication industries. Under the heading "electron tubes," the author includes amplifiers, oscillators, photo-tubes, rectifiers, thyratrons, grid-glow tubes, and cathode-ray tubes. Save for a rather inadequate opening chapter on the fundamentals of electronic tube circuits, the book does not aim to teach the principles and theory of electron tubes. Nor does it, as indeed it could not in view of the magnitude of the subject, pretend to give full technical instructions for putting into practice the various devices considered. For the latter purpose it relies upon references to the original literature, with which it is abundantly provided. The idea of the book is clearly a good one, and so far as the variety and amount of the material treated is concerned the idea has been successfully carried out. But, as is the danger with its type, the book is little more than a compilation. One wishes that the author had not been content only to make a catalogue of extensive factual information and had made some attempt to link up the many examples of the application of electron tubes he gives with principles governing such application. For example, it would have been instructive if the section dealing with the measurement of very low currents and voltages

had been accompanied by a short exposition of the principles on which the devices work. Instead, all that is given usually is a circuit diagram, a few indications of the nature and magnitude of the apparatus used, and a short statement of the results obtainable. Thus the book cannot be fully satisfactory to those to whom it is addressed: to the industrial engineer, because it has insufficient detail, though this, as has already been said, is made up for by reference to the original literature; to the teacher, because the subject is insufficiently analysed; to the student, because by its lack of treatment of principle it is ill-adapted to teach. This is not to say that the book is not a work of great knowledge and labour. Its range is astonishingly varied and the material is much of it of extreme interest. Chapter II. gives a brief survey of available thermionic tubes. Chapter III. is headed "Vacuum-Tube Amplifiers" and concerns such matters as very low voltage and current measurement using circuits of high amplification, voltage and time-delay relays, electronic recorders, etc. Chapter IV. is about "Gaseous Triodes" and various applications of them. Chapters V. and VI. deal with light-sensitive tubes, the general types available, and such applications as control of frequency, temperature and voltage, recorders, speed measurement, etc. The final chapter concerns rectifiers, cathode-ray tubes, and miscellaneous tubes and circuits.

To sum up, while the book has the defect referred to above, it is a valuable record of what has been done with electron tubes outside the wireless industry. It deals with a region which other books on valves tend to neglect, a region whose expansion has made a book of this kind necessary and useful.

K. J.

Lehrbuch der Physikalischen Chemie. By KARL JELLINEK. Stuttgart: Ferdinand Enke. Pp. xxi + 413. Price R.M. 41.

Two sections of Volume V. of this textbook have already appeared and the present section completes the volume. It deals with (1) the structure of molecules, as derived from a study of their dielectric properties, their magnetism and their spectra, (2) the structure of crystals with a section on metals, and (3) the emission and absorption of radiation in physical and chemical processes. The author has surveyed the monographs and literature of the last ten years on these subjects, and has presented his findings in textbook form. The experimental and theoretical aspects of the subjects are emphasised, and in consequence the book contains material not to be found in the usual textbook of physical chemistry. This will make it valuable not only to the student but also to the teacher as well. It should prove to be a happy hunting ground for the writers of more modest textbooks.

This is the last section of the textbook of physical chemistry, which Dr. Jellinek commenced ten years ago. It is a monumental work, extending to nearly 5000 pages, and is a worthy record of the investigations carried out in the borderland between physics and chemistry during the last half-century. It may be that it will prove to be the last of the textbooks on physical chemistry written in the classical style of Ostwald and Nernst. Dr. Jellinek is to be congratulated on his achievement.

W. E. G.

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THE INCREASE IN THE DIPOLE MOMENT OF A DIATOMIC MOLECULE ON DISSOLUTION IN A NON-POLAR LIQUID.

BY FRED FAIRBROTHER.

Received 11th June, 1937.

It has been shown in previous communications ¹ that when hydrogen chloride, hydrogen bromide, hydrogen iodide, or iodine monochloride is dissolved in a nonpolar solvent the dipole moment of the solute is greater than that of the same substance in the gaseous state. This result was interpreted as being due to an increase in the ionic character of the valence bond of the solute molecule. In this paper it is shown that such an increase of moment is to be expected from a consideration of the energies of the states involved, the resonance between the covalent and ionic states and the effect of solvation on the ionic state.

As Pauling ² has pointed out, the quantum mechanics shows that if, for a polyatomic system having a given atomic arrangement, there are two possible electronic states with nearly the same energy and the same multiplicity, then it is necessary to consider mixed states with an eigenfunction for the system formed by linear combination of the eigenfunctions for the first two states. Pauling has illustrated this point in connection with the gaseous halogen hydrides, considerable interaction between the ionic and covalent states being shown to occur in the case of hydrogen fluoride, with progressively less interaction on passing along the halogen series, until in hydrogen iodide the interaction is negligible and the bond almost wholly covalent. Thus, even in the case of molecules like hydrogen chloride and hydrogen bromide in which the energies of the two extreme states are separated by 4 or 5 e. volts, the bond eigenfunction contains ionic terms with small but appreciable coefficients.

Pauling has further suggested ³ that the "extra energy" of bond formation between two unlike atoms A : B, as shown by thermochemical data, over that to be expected for a normal covalent bond on the basis of the covalent bond energies of A : A and B : B is a measure of the ionic nature of the bond A : B and is, in effect, the resonance energy due to interaction between the covalent and ionic states.

Using a similar treatment, the assumption will be made in this paper that the wave function associated with any single bond between unlike atoms can be represented to a first approximation as a linear combination of the wave functions corresponding to the covalent and ionic states

$$\psi = a\psi_{\text{covalent}} + b\psi_{\text{ionic}} \quad \dots \quad (1)$$

¹ Fairbrother, (a) *J.C.S.*, 1932, 43; (b) *ibid.*, 1933, 1541; (c) *Trans. Faraday Soc.*, 1932, 30, 862; (d) *J.C.S.*, 1936, 847.

² *J. Amer. Chem. Soc.*, 1932, 54, 988.

³ *Ibid.*, 3570.

in which the coefficients a and b are normalised, *i.e.* $a^2 + b^2 = 1$. This is an approximate treatment, and the value of the variational integral $\int \psi^* H \psi d\tau$ will lie above the true energy of the molecule, but it will be assumed that this difference is negligible, and hence that any other terms in the linear expansion of ψ can be neglected. It has therefore been assumed that only one ionic form, *e.g.* A^+B^- , is significant, and that the contribution of the corresponding ionic form A^-B^+ to the average molecule is negligible. A more rigorous treatment of the problem would include the consideration of all three forms, namely $A:B$, A^+B^- , and A^-B^+ ; but with the data at present available the solution of the problem along these lines involves other assumptions which probably do not lead to any better approximation than the assumption that the coefficient of the instantaneous inverse dipole A^-B^+ is negligible.

The dipole moment of such a molecule is given by

$$\begin{aligned} \bar{\mu} = e \int \psi^* \sum_{i=1}^n z_i \psi d\tau &= a^2 \mu_{\text{covalent}} + b^2 \mu_{\text{ionic}} \\ &+ abe \int \psi^*_{\text{covalent}} \sum_{i=1}^n z_i \psi_{\text{ionic}} d\tau + abe \int \psi^*_{\text{ionic}} \sum_{i=1}^n z_i \psi_{\text{covalent}} d\tau, \end{aligned}$$

in which z_i is the z co-ordinate of the i th electron from the centroid of positive charge as origin and the moments are measured in the direction of the z , or figure, axis of the molecule. Since we are concerned with the discussion of a single bond, and are neglecting intramolecular polarisation, the z_i 's concerned will be chiefly those of the bonding electrons. The integrals at the right of this expression cannot be given a general evaluation, but although they cannot be neglected altogether they are probably of much less significance than the sum of the first two terms. One may therefore take as a sufficient approximation

$$\bar{\mu} = a^2 \mu_{\text{covalent}} + b^2 \mu_{\text{ionic}}.$$

It would appear to be the most logical procedure to write μ_{covalent} equal to zero and μ_{ionic} equal to the product of the nuclear separation and the electronic charge. This procedure, neglecting polarisation, is really implied in the original approximation of equation (1).

The calculation, moreover, may be simplified by taking

$$H_{cc} = \int \psi_c^* H \psi_c d\tau,$$

the energy of the ground state of the parent completely covalent molecule, as zero, the other energies then being expressed as differences from this state. W (*vide infra*), for example, may be identified as the experimentally determined "extra energy of stabilisation" of the molecule, *i.e.*, the difference (with negative sign) between the actual bond energy and the predicted covalent bond energy.

By substitution of equation (1) in the Schrödinger wave equation $H\psi = W\psi$ and neglecting non-orthogonality of the ionic and covalent wave functions, the variation treatment, minimising with respect to a and b , then leads to the equation

$$\alpha = W \cdot \frac{a}{b} \quad \dots \quad (2)$$

and to the secular determinant

$$\begin{vmatrix} -W & \alpha \\ \alpha & H_{ii} - W \end{vmatrix} = 0,$$

in which $H_{ii} = \int \psi_i^* H \psi_i d\tau$ and $\alpha = \frac{1}{2}(\int \psi_e^* H \psi_i d\tau + \int \psi_i^* H \psi_e d\tau)$ (H being the Hamiltonian operator in each case, and the integration taken over all configuration space), and W is the energy of the lowest state of the molecule.

Expanding the determinant :

$$-WH_{ii} + W^2 = \alpha^2$$

$$\text{or} \quad W = \frac{H_{ii}}{2} \pm \frac{1}{2} \sqrt{H_{ii}^2 + 4\alpha^2}. \quad (3)$$

the two roots corresponding to a lower or actual state of the molecule and to an upper or excited state, which does not enter directly into the present discussion.

From equations (1), (2), and (3), and the experimental values of μ_{average} and W , the value of H_{ii} may be calculated: this is the energy difference between the lowest levels of the parent covalent and ionic states. Any circumstances that would increase the relative stability of the parent ionic state over that of the covalent state for a given value of the internuclear distance, would decrease H_{ii} and lead to a greater ionic character of the bond in question. The effect, for example, of a change in environment on H_{ii} may be calculated, leading to a new value H'_{ii} , from which, since α can be taken as independent of environment,⁴ a new total energy of the lowest level W' can be obtained, and thence, by evaluation of α'^2/b'^2 , the expected change in μ_{average} . This has been done for the effect of dissolution in non-polar solvents on the moments of hydrogen chloride, hydrogen bromide, hydrogen iodide, and iodine monochloride, and leads to predicted values for the moments in solution which agree closely with the experimental values.

In the paper mentioned above,³ the extra, or resonance energy, was calculated as the difference between the bond energy of the molecule $A:B$, as obtained from thermochemical or spectroscopic data and the arithmetical mean of the covalent bond energies of $A:A$ and $B:B$. Recent calculation, however,⁵ makes it appear probable that the geometric mean ($\sqrt{A:A \times B:B}$), instead of the arithmetic mean of the covalent bond energies, may lead to a better value for the predicted covalent bond energy of the molecule $A:B$. These are given in e. volts for the four molecules in question in Table I.

TABLE I.

A:B.	Geometric Mean of Covalent Bond Energies of A:A and B:B.	Actual Bond Energy.	W .
HCl	3.31	4.38	- 1.07
HBr	2.95	3.74	- 0.79
HI	2.61	3.07	- 0.46
ICl	1.946	2.143	- 0.197

⁴ The neglect of the integrals or cross terms of the type $abef\psi_e^* \sum_{i=1}^n z_i \psi_i d\tau$ in the expression for the average dipole moment implies that α does not contain terms which would represent a dipole interaction with the environment, so that to this degree of approximation α is independent of the environment of the molecule.

⁵ L. Pauling and J. Sherman, *unpublished*.

The true covalent bond energy of A:B probably lies between the arithmetic and geometric means of A:A and B:B, but nearer to the latter.

The numerical calculation may be illustrated in the case of HCl. For this molecule $\mu_{\text{average}} = 1.034$, $\mu_{\text{ionic}} = 6.07 D$, and $W = -1.07$ e. volts, whence $b/a = 0.453$ and $H_{ii} = 4.14$ e. volts. This relates to the gaseous state. When the HCl is dissolved in a non-polar solvent, H_{ii} is lowered by the energy of solvation of the dipole. At first sight it might appear that the only electrostatic interaction of the molecule with its surroundings was the interaction of the time-average dipole as ordinarily measured with the field which it induces in the surrounding medium. Calculation of this, however, on any probable model shows that it is far too small to bring about any significant change in the character of the molecule. The assumption, however, that the bond wave function ψ_{AB} can be represented as a linear combination of ψ_{covalent} and ψ_{ionic} implies that at any moment there is a finite probability, measured by the quantity b^2 , that the electronic configuration of the molecule is that of an ion pair. The dipole associated with this ionic configuration will be called the "instantaneous dipole" to distinguish it from the "average dipole" of the molecule. It is the interaction of this instantaneous dipole with the solvent which furnishes the energy of stabilisation of the ionic form. The magnitude of this interaction depends less upon the polar nature of the solvent than might be supposed. The total dielectric polarisation P of a polar solvent may, as is well known, be expressed as the sum of three terms: P_e , the electronic or optical polarisation; P_o , the orientation polarisation of the "permanent dipoles," and a smaller term, P_a , called the atom polarisation (which may be neglected for the purposes of the present discussion). The orientation polarisation P_o is only able to interact to any appreciable extent with the average dipole of the molecules as the times of relaxation ($> 10^{-8}$ sec.) are far too large for the solvent molecules to be affected by an instantaneous dipole which may have a lifetime only of 10^{-15} sec. The optical polarisability, on the other hand, involving only small electronic disturbances, is able to respond to electrical oscillations of high frequency, even of the order belonging to light waves of short wave-length, *i.e.*, of the order of 10^{15} sec. $^{-1}$. For most chemical processes one need only consider the time-average dipole $\bar{\mu} = a^2\mu_{\text{covalent}} + b^2\mu_{\text{ionic}}$, since the movements of atomic masses involved in such processes occur so slowly relative to electronic motions that they are unaffected by instantaneous electronic configurations, and only influenced by the average state of the molecules involved.

In calculating the energy of interaction of the instantaneous dipole with the solvent, therefore, the square of the refractive index of the medium should replace the dielectric constant in the expression for the energy of solvation, calculated on an electrostatic model. In the case of a nonpolar solvent the square of the refractive index for Na light, say, is nearly equal to the dielectric constant, and the latter may therefore be retained in such cases.

It is to be noted that the *total* energy of solvation of the molecule is still small, since it is only the fraction b^2 of the energy of solvation of the instantaneous dipole, and also that the induced field may lag somewhat behind the electronic motions within the molecule leading to a lower solvation energy than the maximum.

Various attempts have been made to calculate the energy of solvation

of a polar molecule; these idealise the shape of the molecule and the location of the dipole. For example, Bell,⁶ using the model of a point dipole of moment μ at the centre of a sphere of radius r_0 and dielectric constant unity, calculated the solvation energy to be

$$\Delta E = -\frac{\mu^2}{3r_0^3} \cdot \left(\frac{D-1}{2D+1} \right),$$

where D is the dielectric constant of the medium: whilst Kirkwood,⁷ using a more rigorous treatment which takes account of the dielectric constant D_i within the sphere surrounding the dipole, has calculated the energy to be

$$\Delta E = -\frac{\mu^2}{r_0^3} \left(\frac{D-D_i}{2D+D_i} + \frac{D_i-1}{D_i+2} \right),$$

which, if D_i is taken as unity, differs from Bell's equation by the factor 3. Since, however, considerable uncertainty still exists as to the magnitude of the parameters involved, in particular of r_0 , the solvation energies in the present paper have been calculated by Bell's equation, on the assumption that $r_0 = r_e$, the nuclear separation.

The equation of Kirkwood, assuming $D_i = 1$, would lead to a higher solvation energy, and hence to a higher predicted value for the dipole moment in solution. Any error involved by the use of Bell's equation would be offset by the errors of other approximations, in particular, that the optical polarisability responds perfectly to the fluctuations of the instantaneous dipole. This interaction can never be more than complete, and it may be very much less.

In this way the energy of solvation of the instantaneous dipole $H+Cl^-$ is calculated to be 0.864 e. volts. Subtracting this from H_{ii} leads to a new value $H'_{ii} = 3.27$ e. volts, and from equation (3) to $W' = -1.236$ e. volts, whence $\mu_{sol} = 1.31$. The remaining data used in the calculations and the results obtained are given in Table II. The

TABLE II.

A:B.	μ Average (gas) Debye Units.	r_e °A.	H_{ii} e.v.	α e.v.	Solvent.	ϵ .	$\mu_{solution}$ Debye Units.	
							Calc.	Experi- mental.
HCl	1.034	1.272	4.14	- 2.36	Benzene	2.283	1.31	1.26
HBr	0.79	1.411	5.15	- 2.17	Benzene	2.283	1.01	1.01
HI	0.38	1.617	8.42	- 2.02	Benzene	2.283	0.46	0.58
ICl	0.8	2.310	2.31	- 0.70	CCl ₄	2.236	1.13	1.49

values of $\mu_{average}$ of the halogen hydrides were taken from Zahn's paper;⁸ the value of the moment of ICl obtained by Luft⁹ by extrapolation of the total dielectric polarisation against $1/T$ was 0.5 D, but, as previously explained,¹⁰ it appears that, on the basis of Luft's polarisation figures and the refractivities of gaseous iodine and chlorine, a more probable value is about 0.8 D. In calculating the solvation energy, v_0 (*vide infra*)

⁶ *Trans. Faraday Soc.*, 1931, **27**, 797.

⁷ *J. Chem. Physics*, 1934, **2**, 351.

⁸ *Z. Physik.*, 1933, **84**, 767.

⁹ *Physic. Rev.*, 1924, **24**, 400.

¹⁰ *J. Chem. Soc.*, 1936, 847.

has been taken as equal to the nuclear separation ν_e . The values for the latter were taken from Jevons' "Report on the Band Spectra of Diatomic Molecules." The experimental values of μ_{solution} are taken from the previous papers of the author.¹

It may be observed that α , which is of the nature of a resonance or exchange integral, is always negative in sign, and that the increase in value of H_{ii} on passing from HCl to HI would be expected in view of the lesser ionic character of the latter.

The calculated values for μ_{sol} are close to the experimental values. The latter lie between values calculated using Bell's equation for the solvation energy, and using Kirkwood's, but closer to Bell's; also the experimental values lie between those calculated on the basis of an arithmetical mean for the covalent bond energies, and a geometrical mean, but closer to the latter, confirming the supposition that other approximations involved are justified.

These conclusions are in accord with the experiments of Plyler and Williams¹¹ on the infra-red absorption of HCl in benzene and of West and Arthur¹² and West and Edwards¹³ on the Raman spectra and infra-red absorption respectively of HCl in non-ionising solvents. All these experiments indicate a small decrease in the vibrational frequency of the dissolved HCl, but much smaller than would account for the observed change in dipole moment if this were due simply to extension of the molecule. In the present discussion it has been pointed out that the electronic resonance must take place without change in nuclear separation. A subsequent slight change in the latter may be expected to occur as a result of the change in type of the valence bond. These considerations also make it appear likely that this effect of the solvent on the dipole moment of a diatomic molecule would be no greater in a polar solvent than in a nonpolar one, since the optical polarisability per unit volume would not be markedly different and the *apparent decrease* of moment due to measurements being made in a polar solvent might even cancel completely the *real increase* due to solvation. This is borne out by the very limited data available: in ethyl bromide ($D = 9.449$) and in ethylene dichloride ($D = 10.580$) the moments of HCl were found to be 1.02 D and 0.97 D respectively.¹⁵

The above treatment shows that the phenomenon under discussion is capable of accounting for the observed changes in dipole moment of the halogen hydrides and iodine monochloride. On the other hand, the uncertainties in the parameters concerned and the approximations involved in the treatment are such that one cannot expect much more than a qualitative agreement.

The question next arises as to why other molecules do not show an increase of dipole moment on transference from the gaseous phase into liquid solution, for much careful work has been carried out by different investigators to show that this is the case where many polyatomic molecules are concerned. In answer to this, it may be pointed out that it is only in the case of a diatomic molecule that the average moment of a molecule can be unambiguously identified with a particular chemical bond. In all other cases the measured moment is a resultant of two or more individual moments. Also the presence on the same atom of other bonds the ionic character of which may be influenced by the presence of

¹¹ *Physic. Rev.*, 1936, 49, 215.

¹² *J. Chem. Physics*, 1937, 5, 10.

¹³ *Ibid.*, 14.

one another means that when such a molecule is transferred from the gas phase into solution, the dipole in question is not transferred from a region of very small polarisability, but the resultant, within the molecule, of the extra molecular field induced by the dipole may add little to the intramolecular field already existent within the molecule. It is possible that this may lie at the root of the anomalies of the carbon-halogen moments, which are so much larger than would be expected on the basis of the relative electronegativities of carbon and the halogens.

Other circumstances, however, such as the formation of an inter-molecular complex with a molecule of the solvent or of another substance, which stabilises the ionic form, may reduce H_{ii} even below H_{cc} , in which case at nuclear separations close to the equilibrium value the ionic structure would contribute more than the covalent, whilst at larger values of nuclear separation the normal state would be represented by a completely ionic structure. This process probably occurs in the Friedel-Crafts reaction in which exothermic formation of an AlCl_4^- ion brings about the "ionisation" of the C—Cl bond.¹⁴

Summary.

The increase in dipole moment which several diatomic molecules exhibit when transferred from the gaseous state to solution has been attributed to an increase in the ionic character of the valence bond. In this paper the secular equation for a bond of mixed type is set up and it is shown that the increase in moment of the molecule can be accounted for by the lowering of the energy levels of the ionic state relative to the covalent state by the solvation effect of the medium.

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Contribution No. 602.

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¹⁴ Cf. Fairbrother, *J. Chem. Soc.*, 1937, p. 503.

THE ELECTRICAL CONDUCTIVITIES OF METALLIC COMPLEXES IN DILUTE SOLUTION.

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It is of interest to interpret the results of conductivity measurements in dilute solution in terms of the sizes of the ions. Owing to their small external fields large ions show less tendency to association,¹ and hence electrolytes composed of large ions should show less tendency to weakness, *i.e.*, they should give linear relations between the equivalent conductivity Λ_e and the square root of the equivalent concentration \sqrt{C}

¹ Bjerrum, *Kal. Danske Vid. Selsk., Mat.-fys.*, 1926, 7, No. 9.

in a greater variety of solvents, and should show better agreement with the Debye-Hückel-Onsager theoretical slopes. The matter is complicated by solvation which in general is more considerable with intrinsically small ions, so that the highly solvated lithium ion is actually larger in some solvents than the relatively unsolvated tetra-ethyl-ammonium ion. But by using the very large ions of metallic complexes it should be possible to obtain results that can be interpreted more simply without the complicating effect of solvation. In addition, since the solvation is less, the actual sizes of such ions will not vary from solvent to solvent, and the mobility values should show better agreement with Walden's Rule.

Cobalt complexes were considered first. A survey of the literature showed that no work had been done at sufficiently high dilution to obtain a linear relation between Λ_c and \sqrt{C} in water. No measurements had been made in organic solvents. After considering sixty-three complex cations and seven complex anions only the salts of the complex anion $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ (Erdmann's Salt) were found to be stable and soluble in organic solvents. (A solubility of at least 10^{-2} mols per litre is desirable, though measurements could be made with solubilities down to 10^{-3} mols per litre.)

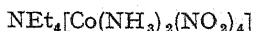
However, a suitable cation was found in the chromium complex ion $[\text{CrPy}_4\text{F}_2]$ which gives stable salts soluble in a variety of organic solvents.

Preparation of Salts.

Potassium diammino-tetranitro-cobaltiate, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, prepared by the method of Werner,² and recrystallised three times from water at 60°C ., was dried *in vacuo* over phosphorus pentoxide at 60°C . (Analysis NH_3 : found 10.90 per cent., 10.82 per cent.; theoretical 10.77 per cent.) The salt gave a clear solution in water, methyl alcohol, acetone and nitromethane, but was not sufficiently soluble in ethyl alcohol or nitrobenzene.

Ammonium diammino-tetranitro-cobaltiate, $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$. The crude salt was prepared by the method of Jörgensen,³ but it was found impossible to purify it by recrystallisation. The crude salt was accordingly converted to the silver salt by precipitation with silver nitrate from aqueous solution. This was recrystallised from a large volume of water at 60°C . (Analysis Ag as AgCl : found 27.6 per cent., theoretical 28.0 per cent.) The silver salt was stirred mechanically for one hour with slight excess of ammonium chloride solution. The filtered liquid was evaporated almost to dryness under reduced pressure at 40°C . The product was recrystallised twice from water at 60°C . It was dried *in vacuo* over phosphorus pentoxide at 60°C . (Analysis NH_3 : found, 17.1 per cent.; theoretical, 17.3 per cent.) The salt gave a clear solution in water, methyl alcohol, acetone and nitromethane, but did not dissolve sufficiently in ethyl alcohol or nitrobenzene.

Tetra-ethyl-ammonium diammino-tetranitro-cobaltiate,



had not previously been prepared. It was made and dried in the same way as the ammonium salt from tetra-ethyl-ammonium bromide (B.D.H. Recrystallised from water).

Analysis.	Found (%)	Theoretical (%)
N	23.92	24.08
H	6.63	6.44

² Werner, *Z. anorg. Chem.*, 1897, 15, 165.

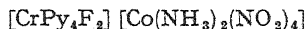
³ Jörgensen, *ibid.*, 1898, 17, 477.

The salt gave a clear solution in water, methyl alcohol, acetone, nitromethane and nitrobenzene, but did not dissolve sufficiently in ethyl alcohol.

Tetrapyridino-difluor-chromic nitrate $[\text{CrPy}_4\text{F}_2]\text{NO}_3$, was prepared by the method of Costachescu.⁴ The chromium fluoride nonahydrate required was prepared by the method of Fabris,⁵ except that it was found that chrome alum could be used satisfactorily instead of the violet chromium sulphate. The nitrate was recrystallised, one sample from water at 60° C., the other from boiling methyl alcohol. It was dried *in vacuo* over phosphorus pentoxide at 75° C. (Analysis NO_3 (using nitron): found, 13.49 per cent.; theoretical, 13.36 per cent.) The salt gave a clear solution in water, methyl alcohol, ethyl alcohol, nitromethane and nitrobenzene, but was not sufficiently soluble in acetone. Measurements made with this salt gave irregular results, indicating impurity. All other salts of this base are prepared by double decomposition from the nitrate, and it is probable that some impurity is removed by this process. Measurements with the nitrate are therefore not included here.

Tetra pyridino-difluor-chromic thiocyanate $[\text{CrPy}_4\text{F}_2]\text{CNS.}$, was prepared by the method of Costachescu.⁴ One sample was recrystallised from water at 65° C., the other from boiling methyl alcohol. It was dried *in vacuo* over phosphorus pentoxide at 75° C. (Analysis, CNS (as AgCNS): found, 12.52 per cent.; theoretical, 12.59 per cent.) The salt gave a clear solution in water, methyl alcohol, ethyl alcohol, acetone, nitrobenzene and nitromethane.

Tetra-pyridino-difluor-chromic tetranitro-diammino-cobaltiate,



had not previously been prepared. It was obtained by mixing 3 per cent. solutions of pure tetra-pyridino-difluor-chromic nitrate and pure ammonium diammino-tetranitro-cobaltiate. The precipitate was recrystallised from a large volume of water at 65° C. It was dried *in vacuo* over phosphorus pentoxide at 65° C.

Analysis.	Found (%),	Theoretical (%).
N	20.31	20.50
H	3.95	3.84
C	35.44	35.13

The salt gave a clear solution in acetone and methyl alcohol, but was not sufficiently soluble in water or ethyl alcohol.

Tetra-pyridino-difluor-chromic perchlorate $[\text{CrPy}_4\text{F}_2]\text{ClO}_4$, was prepared by the method of Costachescu.⁴ It was recrystallised from water at 65° C., and dried *in vacuo* over phosphorus pentoxide at 65° C. The salt gave a clear solution in water but was not sufficiently soluble in organic solvents.

Tetra-pyridino-difluor-chromic picrate $[\text{CrPy}_4\text{F}_2]\text{Pic.}$ had not previously been prepared. It was obtained by mixing solutions of sodium picrate and tetra-pyridino-difluor-chromic nitrate. One sample was recrystallised from a large volume of water at 65° C., but a better yield was obtained by recrystallisation from boiling methyl alcohol. It was dried *in vacuo* over phosphorus pentoxide at 65° C. The salt gave a clear solution in methyl alcohol, ethyl alcohol and acetone, but was not sufficiently soluble in water.

Preparation of Solvents.

Water was prepared by the method of Bourdillon.⁶ Methyl alcohol was prepared by the method of Hartley and Raikes.⁷ Ethyl Alcohol was prepared by the method of Copley.⁸ Acetone was prepared by the method

⁴ Costachescu, *Ann. Scien. Univ. Jassy.*, 7, 87; 8, 16.

⁵ Fabris, *Atti della Reale Accademia dei Lincei*, 1890, 4, 6a, 567.

⁶ Bourdillon, *J. Chem. Soc.*, 1913, 791.

⁷ Hartley and Raikes, *ibid.*, 1925, 524.

⁸ Copley, Murray-Rustu and Hartley, *ibid.*, 1930, 2492.

of Ross-Kane.⁹ Nitrobenzene was purified by redistillation from phosphorus pentoxide, but the results obtained were anomalous, possibly owing to inadequate purification, and are not included here.

Conductivity Measurements.

The method of measuring conductivities was that of Hartley and Barrett.¹⁰ The source of alternating current was a valve oscillator as described by Murray-Rust and Woolcock.¹¹ The thermostat was kept at $25 \pm 0.005^\circ \text{C}$. The cell constant was determined with a solution of potassium chloride in methyl alcohol.

It was found that the diammino-tetranitro-cobaltates were too unstable for accurate measurements in water. The ammonium salt only decomposed very slowly in methyl alcohol, but with the potassium and tetra-ethyl ammonium salts appreciable corrections (*c.* 0.5 per cent. per hour) were required, so that the results are not so reliable. All three salts were stable in acetone. The tetra-pyridino-difluor-chromic salts were found to be stable in all the solvents investigated, but it was necessary to stir during readings in the case of the dilute points; they decomposed slowly in the solid state unless quite dry. All solutions were made up immediately before use.

Experimental Results.

The conductivity results are given in Table I. K is the specific conductivity of the solvent in gemmhos. C is the equivalent concentration. A_e is the equivalent conductivity; the calculated value is obtained from the equation $A_e = A_\infty - \kappa\sqrt{C}$, where A_∞ is the value for the conductivity at infinite dilution, obtained by linear extrapolation, and κ is the observed slope. It is realised that the A_∞ values so obtained are slightly high, but the linear form of extrapolation was used so as to be in accordance with the published data for individual ionic mobilities.¹² When water is added A_e calculated is corrected for the concentration and viscosity changes. $\Delta A_e = A_e \text{ calculated} - A_e \text{ observed}$, and shows how far each individual point falls away from the mean line.

TABLE I—CONDUCTIVITY MEASUREMENTS.

K .	$C \times 10^4$.	A_e .	ΔA_e .	K .	$C \times 10^4$.	A_e .	ΔA_e .
<i>Ammonium diammino-tetranitro-cobaltate in Methyl Alcohol.</i>				<i>Potassium diammino-tetranitro-cobaltate in Methyl Alcohol.^(a)</i>			
0.031	0.9966	99.66	+0.1	0.040	1.0672	93.54	-0.3
	1.8994	98.68	+0.1	0.062	0.5755	94.98	+0.5
	4.8552	96.45	+0.05	0.078	0.4238	94.45	-0.35
	6.6285	95.48	+0.1	0.047	1.0519	93.73	-0.1
0.031	0.5677	100.17	0.0		1.9968	92.73	-0.1
	1.1323	99.41	0.0	0.027	0.8541	94.22	+0.1
	1.8233	98.61	0.0	0.028	0.8272	94.03	-0.1
	2.6941	97.90	0.0		1.6118	93.22	0.0
	3.8310	97.02	0.0		2.3542	92.54	0.0
	5.1478	96.22	0.0				
$[A_\infty = 102.2, \kappa = 264]$				$[A_\infty = 96.5, \kappa = 260]$			

⁹ Ross-Kane, *B.Sc. Thesis, Oxford*, 1929.

¹⁰ Hartley and Barrett, *J. Chem. Soc.*, 1913, 789; Frazer and Hartley, *Proc. Roy. Soc., A*, 1925, 109, 351.

¹¹ Woolcock and Murray-Rust, *Phil. Mag.*, 1928, 5, 1130.

¹² Hartley, Gatty, Macfarlane and Murray-Rust, *Chem. Soc. Ann. Reports*, 1930, 27, 351.

TABLE I.—CONDUCTIVITY MEASUREMENTS (*continued*).

K.	$C \times 10^4$.	Λ_c .	$\Delta\Lambda_c$.	K.	$C \times 10^4$.	Λ_c .	$\Delta\Lambda_c$.
<i>Tetra ethyl-ammonium diammino-tetranitro-cobaltate in Acetone.</i>				<i>Tetra-pyridino-difluor-chromic picrate in Methyl Alcohol (cont.).</i>			
0.017	0.7272	160.97	+0.2	(+0.171% H ₂ O)	8.0727	76.37	+0.4
	1.4211	158.17	+0.2	0.037	1.5349	80.49	-0.05
	2.7159	154.32	+0.1		2.6567	79.50	-0.05
	3.5586	152.31	+0.1		3.6038	78.82	-0.05
	5.0721	149.29	+0.1		5.0908	77.92	-0.04
(+0.266% H ₂ O)	5.0587	148.68	+0.4		7.2852	76.81	-0.02
0.020	0.5694	161.40	-0.2	(+0.178% H ₂ O)	7.2722	76.63	+0.4
	1.1304	158.95	-0.1	$[\Lambda_0 = 83.70, \kappa = 253]$			
	2.6373	153.94	-0.5	<i>Ammonium diammino-tetranitro-cobaltate in Acetone.</i>			
	3.5995	152.06	-0.1	0.013	0.7062	163.94	-0.2
	4.9447	149.36	0.0		1.3054	161.30	-0.1
$[\Lambda_0 = 167.9, \kappa = 830]$					4.6609	152.00	-0.3
<i>Tetra-pyridino-difluor-chromic thiocyanate in Methyl Alcohol.</i>					6.6182	148.40	-0.2
0.031 ^(b)	0.7490	96.06	0.0	(+0.252% H ₂ O)	8.5902	144.45	0.0
	1.2989	95.40	+0.1	0.012	1.1191	162.26	+0.1
	2.2089	94.52	0.0		1.9774	159.02	0.0
	2.9356	93.93	0.0		3.9089	153.90	0.0
	4.1050	93.10	0.0		5.2878	150.96	0.0
(+0.141% H ₂ O)	4.0993	92.77	+0.2		7.5544	147.08	+0.1
0.029 ^(c)	0.7624	95.86	-0.1	$[\Lambda_0 = 171.7, \kappa = 900]$			
	1.4387	95.21	0.0	<i>Potassium diammino-tetranitro-cobaltate in Acetone.</i>			
	2.9611	93.85	0.0	0.018	1.0628	147.76	+0.3
	4.0592	93.04	-0.1		1.8867	145.01	+0.2
	5.7011	92.11	0.0		3.1732	141.78	+0.1
0.019 ^(b)	0.7992	95.96	0.0		4.6089	138.94	0.0
	1.9248	94.67	0.0		6.0621	136.50	0.0
	3.5110	93.33	-0.1		8.6150	133.00	+0.2
	4.9001	92.45	-0.1	(+0.216% H ₂ O)	8.5956	132.83	+0.7
	6.7815	91.42	-0.1	0.018	0.9048	147.78	-0.3
$[\Lambda_0 = 98.3, \kappa = 259]$					1.7975	144.86	-0.2
<i>Tetra-pyridino-difluor-chromic thiocyanate in Acetone.</i>					3.2112	141.09	-0.5
0.044 ^(b)	0.5205	178.9	-0.2		5.9999	136.30	-0.2
	1.0764	176.8	+0.2	$[\Lambda_0 = 155.4, \kappa = 770]$			
	2.2243	173.3	+0.3	<i>Tetra-pyridino-difluor-chromic thiocyanate in Water.</i>			
	3.1038	171.2	+0.4	0.799 ^(b)	0.6542	84.29	-0.1
	4.2667	168.6	+0.2		1.3346	84.08	0.0
(+0.227% H ₂ O)	4.2570	166.7	-0.8		2.4440	83.78	+0.1
0.044 ^(c)	0.5162	179.0	-0.2		3.4336	83.50	+0.1
	1.0236	176.8	0.0		4.7094	83.23	+0.1
	2.1214	173.2	0.0		6.8322	82.78	+0.1
	2.9223	171.1	-0.1	0.701 ^(b)	0.7393	84.25	-0.2
	4.2637	168.3	-0.1		1.7126	83.93	-0.1
$[\Lambda_0 = 184.9, \kappa = 800]$					3.6749	83.31	-0.2
<i>Tetra-pyridino-difluor-chromic picrate in Methyl Alcohol.</i>					4.9932	83.03	-0.1
0.031	1.2881	80.86	+0.03		7.0542	82.60	-0.1
	2.8238	79.51	+0.06		10.053	82.09	-0.1
	4.0120	78.67	+0.04	$[\Lambda_0 = 85.2, \kappa = 95]$			
	5.6244	77.74	+0.07				
	8.0865	76.55	+0.06				

TABLE I.—CONDUCTIVITY MEASUREMENTS (*continued*).

K.	$C \times 10^4$.	A_c .	ΔA_c .	K.	$C \times 10^4$.	A_c .	ΔA_c .
<i>Tetra-pyridino-difluor-chromic thiocyanate in Ethyl Alcohol.</i>				<i>Tetra-pyridino-difluor-chromic picrate in Ethyl Alcohol.</i>			
0.030 ^(b)	0.6763	44.95	-0.15	0.023	0.6276	42.29	-0.12
	1.3453	44.42	-0.1		1.2412	41.77	-0.01
	2.7359	43.51	0.0		2.9539	40.53	-0.02
	3.7735	42.98	0.0		4.0671	39.95	+0.01
	5.4802	42.22	0.0		5.7813	39.14	-0.03
0.030 ^(c)	0.5519	45.02	-0.3	(+0.163% H ₂ O)	5.7719	38.82	+0.15
	1.0501	44.62	-0.1	0.026	1.2409	41.81	+0.03
	1.9375	44.00	0.0		2.3258	41.02	+0.05
	2.6327	43.57	0.0		3.2409	40.41	+0.01
	3.7172	43.00	0.0		4.5009	39.81	+0.06
	5.2599	42.22	-0.1		6.4340	38.96	+0.05
(+0.181% H ₂ O)	5.2504	42.10	+0.1				
[$A_0 = 46.7$, $\kappa = 191$]				[$A^0 = 44.03$, $\kappa = 202$]			
<i>Tetra-pyridino-difluor-chromic perchlorate in Water.</i>				<i>Tetra-pyridino-difluor-chromic diamino-tetranitro-cobaltate in Acetone.</i>			
0.64	1.4697	85.72	0.0	0.065	0.5735	130.45	-0.05
	2.5288	85.40	+0.05		1.2790	128.18	0.0
	3.4215	85.16	+0.05		2.1424	126.11	0.0
	4.8151	84.86	+0.07		2.9290	124.50	0.0
	7.0107	84.41	+0.05		4.0236	122.60	-0.1
0.83	1.3077	85.74	-0.06		5.6786	120.35	+0.05
	2.2600	85.42	-0.02	(+0.244% H ₂ O)	5.6646	119.85	+0.25
	3.1740	85.15	-0.03	0.022	0.5095	130.8	+0.3
	4.3577	84.86	+0.02		1.2728	128.2	0.0
	6.2733	84.44	-0.05		2.2802	125.8	0.0
					3.1314	124.2	0.0
					4.2882	122.3	0.0
[$A_0 = 86.9$, $\kappa = 94.5$]				[$A_0 = 135.3$, $\kappa = 630$]			

^(a) Owing to the instability of the solution single or double point runs were carried out, and corrections applied.

^(b) Recrystallised from Water.

^(c) Recrystallised from Methyl Alcohol.

Agreement with Debye-Hückel-Onsager Equation.

Table II. gives a comparison of the observed and calculated slopes of the conductivity curves. The calculated slopes were obtained from the following equations:

Water	$\kappa = 0.288A_0 + 59.8$
Methyl Alcohol	$\kappa = 0.975A_0 + 158.1$
Ethyl Alcohol	$\kappa = 1.256A_0 + 87.8$
Acetone	$\kappa = 1.650A_0 + 336.6$

Water.—Only $[\text{CrPy}_4\text{F}_2]\text{CNS}$ and $[\text{CrPy}_4\text{F}_2]\text{ClO}_4$ have been investigated. The 25 per cent. divergence from the theoretical slope in both cases is surprisingly large. This is all the more unexpected since the mobility of $[\text{CrPy}_4\text{F}_2]^+$ is lower than would be expected from the value of $l_e \times \eta$ in other solvents.

Methyl Alcohol.—The divergence for $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $[\text{CrPy}_4\text{F}_2]\text{CNS}$, $[\text{CrPy}_4\text{F}_2]\text{Pic}$. are all small. The

complex ions with their low mobilities resemble the highly solvated slow moving lithium and sodium ions, and their salts give better agreement with theory than do those of the faster tetra-ethyl-ammonium ion.

TABLE II.—THE SLOPES.

Salt.	Solvent.	Δ_0 .	Observed Slope.	Onsager Slope.	Per-centage Deviation.
$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Methyl Alcohol	102.2	264	257	+ 4
	Acetone	171.7	900	617	+ 46
$\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Methyl Alcohol	96.5	260	250	+ 4
	Acetone	155.4	770	590	+ 31
$\text{NEt}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Acetone	167.9	830	614	+ 26
$[\text{CrPy}_4\text{F}_2]\text{CNS}$	Water	85.3	99	79	+ 25
	Methyl Alcohol	98.3	259	252	+ 3
	Ethyl Alcohol	46.7	191	146	+ 30
	Acetone	184.9	800	642	+ 25
$[\text{CrPy}_4\text{F}_2]\text{ClO}_4$	Water	86.9	94.5	79.6	+ 25
$[\text{CrPy}_4\text{F}_2]\text{Pic.}$	Methyl Alcohol	83.7	253	238	+ 6
	Ethyl Alcohol	44.0	202	143	+ 29
$[\text{CrPy}_4\text{F}_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Acetone	135.3	630	560	+ 12.5

Ethyl Alcohol.—The divergences for $[\text{CrPy}_4\text{F}_2]\text{CNS}$, $[\text{CrPy}_4\text{F}_2]\text{Pic.}$ are 30 per cent. and 29 per cent. These are of the same order as are given by salts of the alkali metals, in contrast to the tetra-ethyl-ammonium salts which give deviations of the order of 100 per cent., so that the position is similar to that in methyl alcohol.

Acetone.—The divergences for the salts $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{NEt}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $[\text{CrPy}_4\text{F}_2]\text{CNS}$ and $[\text{CrPy}_4\text{F}_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ are 46 per cent., 31 per cent., 26 per cent., 25 per cent. and 12.5 per cent. All other salts investigated, except for $\text{NEt}_4\text{ Pic.}$ with a 34 per cent. deviation showed divergences of over 50 per cent., so that the results emphasised the effect of size in preventing association. The close approach of the double complex salt to the theoretical slope is particularly interesting.

Water Additions.—It will be seen from Table III. that the effect of adding water is always close to that calculated from the concentration and

TABLE III.—WATER ADDITIONS.

Salt.	Solvent.	Per Cent. Water.	Per Cent. Change in Δ_0 Observed.	Per Cent. Change in Δ_0 Calculated.
$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Acetone	0.252	— 0.6	— 0.6
$\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Acetone	0.216	— 0.2	— 0.5
$\text{NEt}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Acetone	0.266	— 0.4	— 0.6
$[\text{CrPy}_4\text{F}_2]\text{CNS}$	Methyl Alcohol	0.141	— 0.3	— 0.5
	Ethyl Alcohol	0.181	— 0.2	— 0.7
	Acetone	0.227	— 1.1	— 0.5
$[\text{CrPy}_4\text{F}_2]\text{NO}_3$	Methyl Alcohol	0.177	— 0.3	— 0.6
	Ethyl Alcohol	0.184	— 0.2	— 0.7
$[\text{CrPy}_4\text{F}_2]\text{Pic.}$	Methyl Alcohol	0.171	— 0.2	— 0.8
	" "	0.178	— 0.2	— 0.8
	Ethyl Alcohol	0.163	— 0.8	— 1.1
$[\text{CrPy}_4\text{F}_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	Acetone	0.244	— 0.4	— 0.6

viscosity changes. In this respect the salts behave like tetra-ethyl-ammonium salts. Such behaviour is considered as evidence of the absence of hydration.¹³

Values for l_0 .—The individual mobilities of the two complex ions are calculated from the Λ_0 figures and the data in the 1930 Annual Reports.¹² These data are based on actual transport measurements in water and the alcohols, but the individual mobilities in acetone depend on the application of Walden's Rule to the picrate ion. It is satisfactory (see below) that the results for the tetra-pyridino-difluor-chromic salts support the mobility previously accepted for the picrate ion in this solvent.

The values obtained for the mobilities in different solvents are given in Table IV. The ion $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$ has a smaller mobility both in methyl alcohol and acetone than any previously investigated, except for the highly solvated lithium ion. The ion $[\text{CrPy}_4\text{F}_2]^+$ appears to have the smallest mobility that has yet been definitely established in water, methyl alcohol, and acetone, but is slightly faster than the lithium ion in ethyl alcohol.

TABLE IV.—MOBILITIES.

$[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$

Solvent.	Cation.	Λ_0 .	l_0 .	l_a .	$l_0 \times \eta$.
Methyl alcohol .	NH_4	102.2	57.9	44.3	0.241
	K ^(a)	96.5	53.7	42.8	
Acetone . .	NH_4	171.7	98.1	73.6	0.232
	K	155.4	82.0	73.4	0.232
	NEt_4 ^(a)	167.9	90.5	77.4	

$[\text{CrPy}_4\text{F}_2]^+$

Solvent.	Anion.	Λ_0 .	l_0 .	l_a .	$l_0 \times \eta$.
Water . . .	CNS	85.3	65.4	19.9	0.177
	ClO_4	86.9	67.0	19.9	0.177
Methyl Alcohol .	CNS	98.3	61.0	37.3	0.203
	Pic.	83.7	46.7	37.0	0.202
Ethyl Alcohol .	CNS	46.7	29.2	17.5	0.191
	Pic.	44.03	26.8	17.2	0.188
Acetone . . .	CNS	184.9	123.4	61.5	0.194
	$[\text{CoNH}_3)_2(\text{NO}_2)_4]$	134.64	73.5	61.1	0.193

^(a) This value for l_0 is less reliable owing to decomposition of the salt.

^(b) Certain other tetra-ethyl-ammonium salts give anomalous mobilities in acetone.

Walden's Rule.—The values for the product $l_0 \times \eta$ are given in the last column of Table IV. $l_0 \times \eta$ is constant to within 5 per cent. for $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$ in acetone and methyl alcohol, and for $[\text{CrPy}_4\text{F}_2]^+$ in methyl alcohol, ethyl alcohol and acetone. This is better agreement than is given by the tetra-ethyl-ammonium ion.

The small value of $l_0 \times \eta$ for $[\text{CrPy}_4\text{F}_2]^+$ in water (it is 25 per cent. lower), suggests that in this solvent the complex ion is solvated; co-ordination to water might occur from the nitrogen in the pyridine, or from the fluorine.

Summary.

1. The following new salts have been prepared: Tetra-ethyl-ammonium diammino-tetranitro-cobaltiate, tetra-pyridino-difluor-chromic diammino-tetranitro-cobaltiate, tetra-pyridino-difluor-chromic picrate.

2. The electrical conductivities have been measured of solutions of some diammino-tetranitro-cobaltiates in methyl alcohol and acetone, and of some tetra-pyridino-difluor-chromic salts in water, methyl alcohol, ethyl alcohol and acetone.

3. (a) Values have been obtained for $l[\text{Co}(\text{NH}_3)_2(\text{NO}_3)_4]$ in acetone and methyl alcohol, and for $l[\text{CrPy}_4\text{F}_2]$ in water, methyl alcohol, ethyl alcohol and acetone.

(b) The relation between Λ_c and \sqrt{C} is in fairly close agreement with Onsager's equation for all the salts investigated.

(c) The effect of water additions is in agreement with that calculated from the changes in concentration and viscosity.

(d) The value of $l_0 \times \eta$ is constant to within 5 per cent. for the ion $[\text{Co}(\text{NH}_3)_2(\text{NO}_3)_4]^-$ in acetone and methyl alcohol, and for the ion $[\text{CrPy}_4\text{F}_2]^+$ in methyl alcohol, ethyl alcohol and acetone, but is 25 per cent. lower for the latter ion in water.

The author expresses his gratitude to Sir Harold Hartley who suggested the measurements, to Dr. D. M. Murray-Rust for advice and experimental assistance, to Dr. C. W. Davies for encouragement and permission to finish the work at Battersea Polytechnic, and to Dr. R. P. Bell for advice.

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ON THE PRINCIPLE OF PRIMARY RE-COMBINATION IN RELATION TO THE VELOCITY OF THERMAL REACTIONS IN SOLUTION.

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It has often happened that the study of photochemical reactions has thrown light on the corresponding thermal processes, particularly where the mechanism of chain reactions is concerned; but photochemistry has up to the present been less successful in elucidating the more fundamental questions relating to the nature of the velocity coefficient of thermal reactions. Mr. Bamford and I have, however, recently obtained quantitative results which appear to have a special interest in this connection, and it is proposed in this paper to give a brief summary of

these results together with the conclusions relating to the velocity coefficient in solution which may be drawn from them.

It is well known that reactions in general are subject to a temperature independent factor which measures the deviation of the velocity coefficient from that calculated from the simple theory of kinetic activation. For a simple bimolecular reaction this can be expressed by the relationship

$$\text{velocity} = PZe^{-E/RT},$$

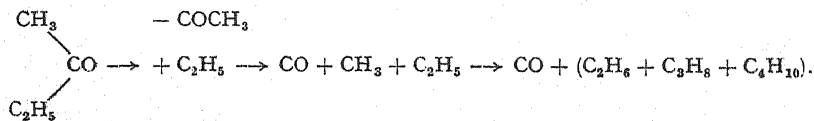
where Z is the total number of collisions between reactant molecules, E the Arrhenius activation, and P is a probability factor. More generally, we may write

$$\text{velocity} = P (\text{number of activating collisions}).$$

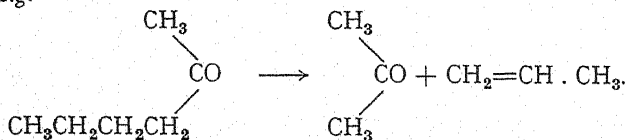
For some reactions P is appreciably unchanged as we pass from gas phase to solution or from solvent to solvent, and may for simple reactions be of the order unity. This class of reaction is distinguished as "normal." For another group of reactions in solution, however, P has not only a small value of 10^{-3} to 10^{-11} , but varies widely from solvent to solvent,⁷ becoming smaller as the polarity of the solvent decreases. Such reactions have been termed "abnormal." These definitions should be carefully noted in view of the argument which follows. An understanding of the reason for this great reduction and variation in the probability factor P for such reactions is obviously of fundamental importance to the interpretation of these thermal processes in solution. Thus any experimental evidence of direct application has a special interest. Such evidence is afforded by our comparative study of the quantum yields of photodecompositions of aldehydes and ketones in the gas phase and in solution, of which the following is a summary:¹

Ketones in the gas phase may decompose under the influence of ultra-violet light of wave-length 3000 A.U. in two ways:

Type (I) predominant among compounds with short hydro-carbon chains, involves the elimination of carbon monoxide, and the formation of free radicals, *e.g.*

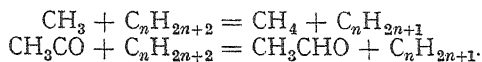


Type (II) predominant among compounds with long hydrocarbon chains involves a cracking of the hydrocarbon chain in the position α - β with reference to the carbonyl group, with the formation of an olefine, *e.g.*

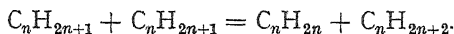


¹ Norrish and Kirkbride, *J. Chem. Soc.*, 1932, 1518; Norrish and Appleyard, *ibid.*, 1934, 874; Norrish, *Trans. Faraday Soc.*, 1934, 30, 107; Norrish, *Acta. Physica Chemica U.R.S.S.*, 1935, 3, 171; Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1934, 1456; Bamford and Norrish, *ibid.*, 1935, 1504; Spence and Wild, *Nature*, 1936, 138, 206; Norrish and Bamford, *Nature*, 1936, 138, 1016; 1937, 140, 195.

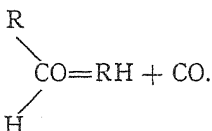
When these reactions are carried out in solution in liquid paraffin, or in *iso*-Octane, type (I) reaction is modified by the hydrogenation of the free radicals. Thus, with methyl ethyl ketone, methane, ethane, acetaldehyde and carbon monoxide are produced almost exclusively, and there is no recombination of free radicals to form higher paraffins. The free radicals react with the solvent by reactions of the type



This is confirmed by the quantitative development of an unsaturation in the hydrocarbon solvent due to a disproportionation reaction between free radicals which after removal of the carbonyl substances can be titrated with bromine water :



On the other hand, type (II) reaction occurs in solution without modification. These results have been confirmed for a considerable number of ketones, *i.e.* methyl ethyl, diethyl, methyl butyl, di-*n*-propyl, and di-isopropyl ketones. With aldehydes similar results are obtained, but in this case, the reactions of type (I) are much less modified in solution. This is due to the fact that very few free radicals are formed in the decomposition of aldehydes, the process occurring mainly in one act with the production of only one hydro-carbon



In consequence of this, very little unsaturation is produced in the solvent by the photodecomposition of aldehydes.

It was when the quantum yields of these processes were compared in the gas phase and in solution that a result came to light which appears to have important bearing on the wider problem referred to above.²

Di-*n*-propyl ketone decomposes by both types of reaction. In the gas phase, using light of wave-length 2400-2800 A.U. the quantum yield is 0.37 for type (I) and 0.29 for type (II) measured

QUANTUM YIELDS OF DI-*n*-PROPYL KETONE.

Gas.			
Temperature °C.	20	70	100
Type (I) reaction (CO)	~0.3	0.36	0.37
Type (II) reaction (C ₂ H ₄)	~0.3	0.30	0.29
<i>iso</i> -Octane Solution.			
Temperature °C.	20.5	68	96
Type (I) reaction (CO)	0.01	0.17	0.30
Type (II) reaction (C ₂ H ₄)	0.23	0.19	0.175

by the yields of carbon monoxide and ethylene respectively. This is unchanged over the range of temperature 70 to 100° C., and no formation of diketone can be detected between these temperatures. At 20° C. both the reactions continue with quantum yields of the same order though type I is associated with the production of diketone owing to the comparative stability of the C₃H₇·CO radical at the lower temperature. In solution, however, the quantum yield of type (I) reaction is subject to a marked temperature effect and at room temperature is reduced to *an extremely*

² Details shortly to be published (Bamford and Norrish).

small value, while for type (II) reaction the quantum yield is nearly the same as in the gas phase and only slightly affected by temperature.

If we fix our attention on the figures for room temperature we may contrast the enormous drop in the quantum yield for the type (I) reaction when carried out in solution, with the relative constancy of the quantum yield of the type (II) reaction. Thus from a single substance there arise concurrent reactions which follow respectively the behaviour of the two types of thermal reactions in solution. One is forced to the conclusion that virtually the whole of the reaction in solution according to type (I) is dependent on the hydrogenation of the free radicals by the solvent. This is a temperature dependent process, and at low temperatures where it occurs with great inertia, the reaction in solution is almost completely suppressed.

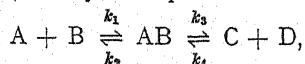
We have here a remarkable example of the Franck-Rabinowitsch principle of primary recombination,³ and throughout the progress of the work we have continually had impressed on us the great fundamental importance of this concept. According to this idea, the free radicals formed, for example, by decomposition of a ketone in solution are virtually enclosed in a cage or shell of solvent molecules, and unless these free radicals can be removed by reaction with the solvent or by decomposition, recombination to form the ketone is almost inevitable.

With the reaction of type (II) however, the photodecomposition produces not free radicals, but finished molecules, and as there is now no affinity for recombination the Franck-Rabinowitsch principle does not apply; the reaction proceeds with nearly unabated vigour in solution nearly independent of temperature.

There is a similar marked contrast when we compare the reactions of type (I) of aldehydes with those of ketones. In the case of aldehydes (e.g. isovaleraldehyde) even down to the temperature of -80°C . there is a ready decomposition in solution, while with dipropyl ketone, as we have seen, the quantum yield rapidly approaches zero. Here again, in the case of aldehydes, since finished molecules are produced by the decomposition, the Franck-Rabinowitsch principle will not operate, and the stabilisation of the process will not be dependent on the fixing of free radicals by secondary reaction.

Thermal Reactions.

Under certain conditions this principle, now well established for photochemical reactions, will extend to thermal reactions in solution. It has been shown that many such reactions may be visualised in terms of the decomposition of a transition complex. Such a transition complex may decompose in either of two ways—to give original reactants or to give new products. This may be represented as follows:



and the velocity of the reaction is given by the equation:

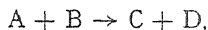
$$\text{velocity} = \frac{k_3(k_1[A][B] + k_4[C][D])}{k_2 + k_3}.$$

From the calculations of Rabinowitsch and Wood⁴ it is clear that the particles A and B or C and D generated by the decomposition of the

³ Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120.

⁴ Rabinowitsch and Wood, *ibid.*, 1936, **32**, 1381.

transition complex will make on the average two or three subsequent collisions before separating owing to their confinement by the solvent molecules. This will effectively reduce both k_2 and k_3 , but since each will be effected to the same extent, there will be no resultant effect on the overall reaction velocity of



which, if k_4 is small—(*i.e.* negligible back reaction) will be bimolecular and given by

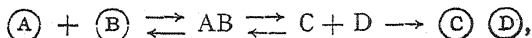
$$\text{velocity} = \frac{k_1 k_3}{k_2 + k_3} [A][B].$$

Such a reaction, in which C and D are produced as finished molecules which do not require stabilisation by the solvent, may be termed a normal reaction. Its velocity will not vary appreciably from solvent to solvent, nor from solvent to the gas phase. Many such reactions have been described: if in addition k_2 is small compared with k_3 , the equation for the velocity simplifies to

$$\text{velocity} = k_1 [A][B],$$

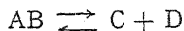
and in simple cases k_1 will be calculable from the collision theory of reactions. It should be emphasised, however, that while the probability factor P for such reactions may be small, due to the smallness of the factor $\frac{k_3}{k_2 + k_3}$ (transmission factor greatly less than unity) it will not vary appreciably from solvent to solvent and from solvent to homogeneous gas phase.

It is very different, however, if the immediate products C and D require stabilisation by the solvent. This will be the case for nascent ions requiring stabilisation by solvation or free radicals requiring stabilisation by hydrogenation or some similar reaction. Our scheme now becomes modified as follows:



where the circles represent stable reactants or resultants.

The nascent products C and D will be imprisoned in a "Franck-Rabinowitsch cage" making several mutual collisions before they finally separate. Formally no great distinction need be made between the transition complex AB and the nascent products C + D, and the process



can now be regarded as a vibration of the transition complex which does not lead to final reaction unless either C or D became stabilised by the solvent. Thus we may regard the life of the transition complex as greatly extended by the operation of the Franck-Rabinowitsch principle. While in this state, there are two alternative fates which may overtake the transition complex—either (1) it may be deactivated by collision with solvent molecules and the removal of its energy will result in the regeneration of stable molecules \textcircled{A} and \textcircled{B} ; or (2) it may stabilise to \textcircled{C} and \textcircled{D} by the reaction of either C or D or both with the solvent.

Let τ_1 be the mean life of the transition complex as extended by the operation of the process described above; this will depend on the internal

pressure of the solvent, and will not vary greatly from solvent to solvent. Let τ_2 be the potential mean life of the shorter-lived nascent ion C or D if it could be isolated in the solvent medium (*i.e.* the time required for its solvation). This will obviously vary with the polarity from solvent to solvent. Then, formally one can write

$$\text{Probability of stabilisation} = \frac{\frac{1}{\tau_2}}{\frac{1}{\tau_2} + \frac{1}{\tau_1}} = \frac{\tau_1}{\tau_1 + \tau_2}.$$

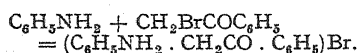
This means that the reaction rate of bimolecular reaction, as given above, will be modified by a probability factor $\frac{\tau_1}{\tau_1 + \tau_2}$, and the velocity will become

$$\text{velocity} = \frac{k_1 k_3}{k_2 + k_3} \frac{\tau_1}{\tau_1 + \tau_2} [A][B].$$

Now, in a highly non-polar solvent, where the tendency to solvation of ions is slight τ_2 the potential mean life of the nascent ion will be very great (infinite in the case of an ideal non-polar solvent) and thus since τ_1 is small and nearly constant the probability factor for the reaction may assume a very small value. For a highly polar solvent, however, τ_2 may be of the same magnitude as τ_1 , and the probability factor due to solvent effect will be of the order unity.

Such reactions which have a very small probability factor in non-polar solvents, and whose probability factor varies markedly from solvent to solvent have long been known, and may be termed abnormal.

TABLE I.—REACTION BETWEEN ANILINE AND BROMACETOPHENONE IN VARIOUS SOLVENTS.*



Temperature 38° C.

Solvent.	<i>P</i> .
Benzene . . .	4×10^{-11}
Chloroform . . .	6×10^{-9}
Acetone . . .	1.7×10^{-7}
Nitrobenzene . . .	4.0×10^{-6}
Methyl alcohol . . .	4.3×10^{-6}
Ethyl alcohol . . .	3.9×10^{-5}
Butyl alcohol . . .	3.9×10^{-5}
Benzyl alcohol . . .	4.9×10^{-5}

* (Cox.)⁶ (For calculation of *P* see Norrish and Smith.⁷)

As examples we may cite the Menchutkin reactions and the hydrolysis of acetic anhydride. In Table I are shown a few figures illustrating the great variation on *P* for such a reaction from solvent to solvent, and also the fact that *P* is smallest for non-polar solvents, as is required by the present theory. It must be placed on record that the experiments which show that these reactions proceed with similarly small probability factors in the gas phase⁵ are valueless to the present argument. They only show that for such reactions in the gas phase the probability factor is zero for the homogeneous reaction, and that the reaction takes places instead on the surface of the containing vessel. The reason for this is obvious when it is remembered that the two reactions in question involve ionic stages which are effectively excluded from homogeneous

⁵ Moelwyn-Hughes and Hinshelwood, *J. Chem. Soc.*, 1932, 230; Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford, 1933, pp. 109, 110.

⁶ Cox, *J. Chem. Soc.*, 1921, 119, 142.

⁷ Norrish and Smith, *ibid.*, 1928, 129.

gas reaction. Thus the argument of Moelwyn Hughes and Hinshelwood,⁵ that the slowness of slow reactions in solution cannot be ascribed to deactivating effects of the solvent requires modification, and is only true for the class of normal reaction described above. In this normal class are the decomposition reactions of Cl_2O , O_3 and the various Diels-Alder reactions in which finished molecules which do not require stabilisation are produced. They take place with velocities which remain sensibly unchanged as we pass from gas phase to solution or from solvent to solvent. Any probability factor to which such reactions are subject will be due to the operation of causes entirely unconnected with the solvent, such as the necessity of internal phase relationships in the case of complicated molecules, and requirements of orientation.

Where the probability factor of a reaction varies widely from solvent to solvent we have a clear criterion of abnormality. Such reactions are not subject to the above statement of Moelwyn Hughes and Hinshelwood; their products require stabilisation by the solvent, and due to the causes described above, the transition complex is subject to varied deactivating effects by different solvents.

The Effect of Pressure on Reaction Velocity.

It has been shown by Perrin⁸ and his collaborators that there is a very great difference in the effect of pressure upon the velocity of normal and abnormal reactions. With normal reactions, the application of pressures up to 10,000 atmospheres leaves the temperature independent factor P practically unchanged. With abnormal reactions (the Menshutkin reactions), however, similar variation of the hydrostatic pressure involves a variation in the probability factor of some 20 to 100 fold. This follows readily from the Franck-Rabinowitsch principle. For normal reactions the velocity given by the equation:

$$\text{velocity} = \frac{k_1 k_3}{k_2 + k_3} [A][B]$$

will be unchanged, since pressure operating through the Franck-Rabinowitsch principle affects equally the coefficients k_2 and k_3 and leaves k_1 , which depends on the number of collisions between A and B practically unchanged. (By the operation of the Franck-Rabinowitsch principle the collisions between A and B will tend to occur in groups, but their total number will be only slightly affected, as the hydrostatic pressure is increased.) For abnormal reactions, however, the velocity is given by

$$\text{velocity} = \frac{k_1 k_3}{k_1 + k_3} \frac{\tau_1}{\tau_1 + \tau_2} [A][B]$$

and of the factors affecting this equation τ_1 the life of the activated complex (including the period during which the nascent products C and D remain close in contact by the operation of the Franck-Rabinowitsch principle) is markedly increased by increase of hydrostatic pressure due to the decrease in free space available to the solute. On the other hand, τ_2 the potential life of the nascent ion isolated in the solvent is practically independent of pressure. Thus, for reactions in inert solvents when τ_2 will always be much greater than τ_1 , the probability factor will be approximately τ_1/τ_2 and will be markedly dependent on pressure.

⁸ Perrin, *Proc. Roy. Soc., A.*, 1936, **154**, 684; 1937, **159**, 162.

Thus, by a consideration of the Franck-Rabinowitsch principle in conjunction with the stability or necessity of stabilisation of the reaction products, we obtain a natural division of thermal reactions in solution into just those two classes which have been previously distinguished experimentally and an explanation of the remarkable difference in the effects of pressure on the two classes.

It should be emphasised that the considerations discussed in the present paper are not the sole causes affecting the temperature independent factor of the reaction velocity coefficient; it may be claimed, however, that they do show one reason for variation of this factor from solvent to solvent and from solvent to gas phase for those reactions classed as abnormal. Other requirements such as necessities of orientation and the internal phase relationships of the reacting molecules will play their part in fixing P for a given reaction, but such influences will operate to a first approximation equally in the gas phase and in solution and will not differentiate solvent from solvent. They are not the cause of "anomalies" found among reactions in solution.

Summary.

Examples are given of the operation of the Franck-Rabinowitsch principle of primary recombination on the photo-decomposition of aldehydes and ketones in solution. For reactions in which free radicals are formed there results an enormous reduction of quantum yield as we pass from the gas phase to solution, but little change occurs with reactions which produce finished molecules. The results are generalised for thermal reactions and indicate an explanation of the differentiation of reactions in solution into the two classes "normal" and "abnormal." The differing effects of hydrostatic pressure on these two classes of reaction readily follow.

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MEASUREMENT OF SPEED OF SPREADING OF DROPS OF AQUEOUS SOLUTIONS ON MERCURY.

BY R. S. BURDON, G. R. FULLER AND E. S. H. GIBSON.

Received 11th October, 1937.

A cinema camera has enabled measurements of the rate of spreading to be made, as suggested in a paper some years ago.¹ The technique has enabled the process of spreading to be followed but cannot be said to have confirmed any particular theory as to the mechanism of spreading.

Visual observations show that a drop of pure water spreads slowly on mercury, whereas a solution of an acid as dilute as one-ten-thousandth normal spreads within a second to a circle of which the area is proportional to the amount of acid in the drop. From this it seems necessary that practically every ion (or molecule) of the acid must react in some way at the interface during the rapid stage of spreading. If the ions in the

¹ *Trans. Faraday Soc.*, 1927, **23**, 205.

solution reach the mercury only at the advancing edge of the drop, then the rate of spreading might be expected to be most rapid at the start. If, however, spreading is due to ions coming into the interface at any point, as heat movements happen to cause openings among the ions already at the mercury surface, then the number of new ions to reach the mercury will depend on the area of the interface, or the rate of spreading at any instant should depend on the area already covered. It was thought from visual observations that such accelerated spreading did occur.

Experimental Method.

A properly cleaned glass dish about 10 cms. in diameter was used. After focussing the camera, clean mercury was poured into the dish, and half a minute later the camera was started and a drop of solution placed on the middle of the mercury surface. It was found that a light dusting of lycopodium just before putting on the drop made very little difference to the spreading and greatly helped in defining the drop in the photos. The camera gave pictures equally spaced at 16, 24 or 32 per second as desired. After development the film was placed in a projector, so arranged that the pictures were natural size. The diameter of the drop was then simply measured with a scale as the successive pictures were thrown on the screen.

Results.

Measurements at once showed that the phenomena were even more regular than had been judged by eye, small fluctuations in speed occurring at just the same stage when successive drops were photographed under similar conditions.

In the graphs, diameter of drop is plotted against time. Fig. 1 A is the curve for a drop of approximately 10^{-4} N HCl, and shows the sudden fall in speed when the drop has covered the area determined by the acid content. The rate falls from 4.5 cm./sec. to 0.25 cm./sec. in less than one-tenth of a second.

Curve B is for a drop of double the concentration of A and the diameter grows at 5.7 cm./sec. Measurements show that, particularly for drops of higher concentration (Curve C), the spreading rate is slightly accelerated as suggested above, but the effect is small and the outstanding fact is the nearly uniform rate at which the diameter grows from the start until the rapid stage is ended.

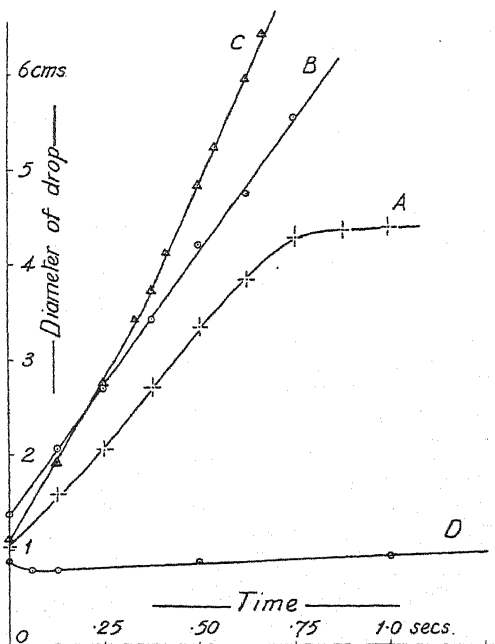


FIG. 1.

Curve D is for a drop of distilled water; it shows an apparent contraction for the first three pictures and provides evidence that could not be gained by visual observations as to this stage of spreading. The drops flatten out as they strike the mercury, and in the case of an acid continue to spread, but there are not sufficient ions immediately available in the drop of pure water for it to wet the area to which the drop is spread by its momentum and so a contraction occurs at first. Thereafter it spreads slowly as ions become available.

In Fig. 2 are shown E, the rate of spreading of conductivity water on mercury, and F, the rate for conductivity water to which a trace of tap-water was added. In these the diameters were measured directly over a period of some minutes. In each case the slow spreading is at a uniform rate, the trace of tap-water giving a more rapid stage at first until most of the ions from the impurities were absorbed. For the pure water the rate of growth of the diameter was only about 0.3 mm. per second. Obviously

in each case the periphery advances at half the speed given.

A drop of aqueous solution on mercury then spreads so that the edge advances at a steady rate. The area increases at a rate that is proportional to the length of the circumference, and practically independent of the area already covered. This holds for pure water and for solutions that spread more than a hundred times as fast as pure water. More concentrated drops spread more rapidly and do show a slight acceleration, but doubling the concentration only increases the rate by about 25 per cent.

For a given concentration a large drop was found to spread more

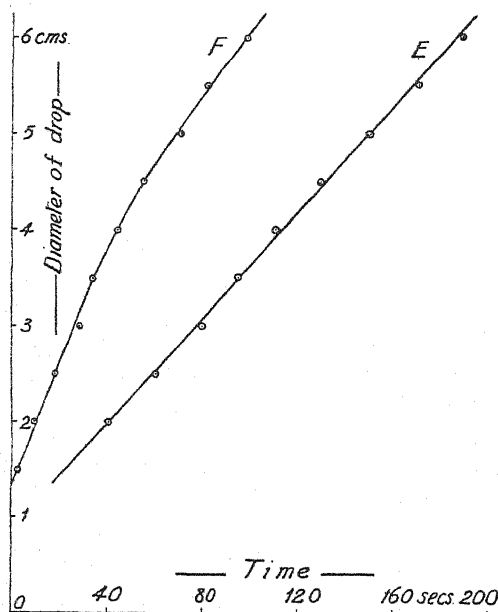


FIG. 2.

rapidly than a small one. This suggests that the larger bulk of liquid flows more readily and so permits more rapid spreading, but such an explanation is not in accord with the fact that for any given drop the edge advances at nearly the same speed from the start until it has spread to a disc less than one-thousandth of an inch thick, when viscous resistance should be apparent. The constant speed seems to indicate that the spreading rate is determined almost completely by processes occurring at the advancing edge of the drop and not over the interface. The persistence of this speed so long as ions are available (Curve A) suggests a constant spreading pressure depending on the nature of the drop, opposed by a resistance which is determined by the mercury. A theory which accounts for this, however, cannot be made to fit the fact that for a given concentration a large drop spreads faster throughout than a small one.

Relative measurements were made on the interfacial tension of mercury against pure water and very dilute acid and alkaline solutions respectively. As was expected from their non-spreading, alkalis increase the interfacial tension. Acids, even at extreme dilution, cause a reduction of the inter-

facial tension, giving a positive spreading coefficient. It is not possible, however, to measure the interfacial tension during the stage of rapid spreading in order to find if a simple relation holds between spreading coefficient and speed.

The tendency for a drop to continue spreading at a uniform speed contrasts with the rapid fall of speed with increasing area found by Landt and Volmer,² when small drops of olive oil spread over large water surfaces.

Summary.

Photography shows that, for a given concentration a drop of aqueous solution spreads at nearly uniform speed on mercury. The speed is greater for more concentrated drops, and is accelerated slightly as the drop reaches a diameter of about 3 cm.

The spreading is conditioned by the interface, alkaline solutions having a greater interfacial tension against mercury than pure water, while acids, even at extreme dilution, reduce the interfacial tension.

Adelaide.

² *Z. physik. Chem.*, 1926, **122**, 398.

SPREADING WITH UNIFORM ACCELERATION.

BY W. D. ALLEN, KERR GRANT AND R. S. BURDON.

Received 11th October, 1937.

Spreading of Paraffin Irradiated with Ultra-Violet Light or containing Traces of Fatty Acids.

In experiments made some time ago it was found that drops of pure heavy paraffins which normally do not spread on water could be caused to do so if they were irradiated with ultra-violet light. The phenomena presented during spreading were studied both when the drop was placed on the water and then irradiated and when the oil was irradiated first and then placed on the water. The change produced in the paraffin by ultra-violet radiation seems permanent, since oil thoroughly irradiated and then kept for some months was found to spread on water. Similar observations are reported by Stenstrom and Vigness.¹ The appearance presented by a drop of the irradiated oil while spreading is closely duplicated by the spreading of oil containing a small concentration of stearic acid. The close parallelism suggests that the action of the ultraviolet light in air is to produce fatty acids in the paraffins, but it is found that oil irradiated in a quartz container in the complete absence of air is still rendered capable of spreading on water.

It seems clear that the spreading is controlled by the adsorption at the interface of the molecules which have been changed by the radiation. It was decided to test the suggestion that the rate of increase of area should be proportional to the area already covered (see previous paper). Readings taken on the slowly spreading drop at intervals of 20 seconds showed approximately the expected acceleration. More precise readings

¹ Langmuir, *J. Frank. Inst.*, 1934, **218**, 143.

were obtained by measurements on photographs taken at these intervals. These readings showed that in the early stages of spreading the acceleration was given by the relation

$$dA/dt = \text{const} \times A,$$

where A is the area covered at the instant considered. This is in agreement with the formula derived by Langmuir² for small areas, *viz.*:—

$$d. \log A/dt = \text{const.}$$

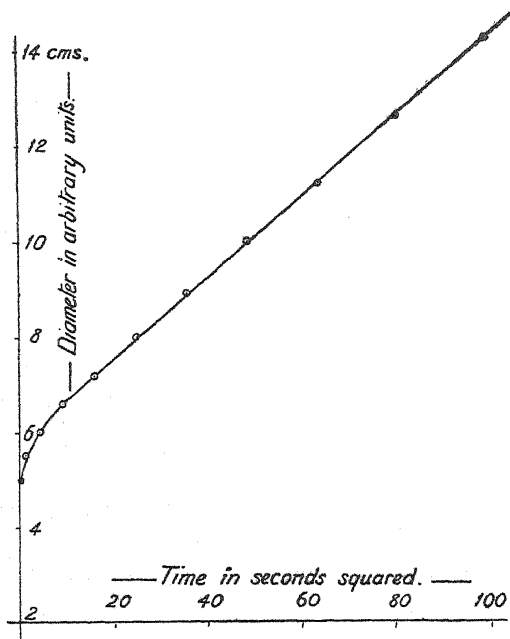


FIG. 1.

After the diameter of the drop had reached approximately 1 cm., however, it was found that an exact linear relationship held between the diameter and the square of the time or the diameter, grows with constant acceleration. How closely this relationship holds is shown by the graph (Fig. 1) which shows the diameter of the drop plotted against the square of the time.

It is obviously not a case of a constant spreading force producing constant acceleration, since at such slow speed, owing to viscous effects, the speed and not the ac-

celeration would be proportional to the instantaneous value of the force. The accuracy of fit of the points, however, indicates that the square law really holds over this stage of spreading and is not merely an approximation.

Adelaide.

² Stenstrom and Vigness, *J. Chem. Physics*, 1937, 5, 298.

HEAT OF COMBINATION OF LIQUID BASES WITH LIQUID ACIDS TO FORM LIQUID SALTS: PIPERIDINE AND SOME ALIPHATIC ACIDS.

BY E. B. R. PRIDEAUX AND R. N. COLEMAN.

Received 31st August, 1937.

In a series of papers¹ relations have been studied between the densities, surface tensions (parachors), viscosities and conductivities of the salts and mixtures formed by the lower fatty acids (propionic to octoic), with the strong bases, piperidine and diethylamine.

The changes of these properties on combination were studied, not only in the solvent-free systems but also dissolved in benzene (typical cases), and the chief characteristics of the salts in aqueous solution have also been determined. Such systems are uniquely fitted to determine the effect on these properties of the passage of a proton to the pure or solvated base.

More or less pronounced maxima of D , σ , η and λ at or near the salt composition (in mixtures which were varied continuously) suggest stoicheiometrical combination of the monobasic acids with the monacid base. Deviations of the maxima from these exact compositions were accounted for by unsymmetrical molecular dissociation. In the case of surface tension, a further factor was surface adsorption. Whether the intensities of these maxima are characteristic of completely ionised salts cannot be definitely stated, since few, if any, salts of the highly ionised type have been investigated which are liquid at the same temperatures as their constituent acids and bases.

Molar conductivities of fused organic salts are roughly proportional to the dissociation constants of the acids and bases (in aqueous solution).^{1(b)} Thus, tetrapropyl-ammonium picrate gives $\lambda = 5.188$ (at 150°) piperidine propionate $\lambda = 0.0851$ at 25°. A few examples may be found in which viscosities and temperatures are more nearly equal, thus:

	$t^{\circ}\text{C.}$	η .	λ .
Piperidine heptoate . . .	60°	0.214	0.0627
Triamylammonium picrate ²	120°	0.2165	0.197

Affinities of formation are also proportional to heats of formation, since A nearly = Q for reactions between condensed phases at room temperatures. Salts with high conductivities appear to have high heats of formation and *vice versa*. Examples will be given later. Since the conductivities of the present series have been determined, a comparison of the heats will show whether this proportionality extends to finer differences (in conductivity).

When piperidine is mixed with the lower fatty acids, either in the pure state or in solution in benzene, considerable amounts of heat are

¹ *J. Chem. Soc.*, (a) 1936, 1346; (b) 1937, 4; (c) 1937, 462; (d) 1937, 1022.

² See especially Walden, Ulich and Birr, *Z. physik. Chem.*, 1928, 131.

evolved which must represent the decrease of total energy when a proton is transferred from the undissociated acid to the anhydro-base. Any differences in the heats must be due to differences in the energy with which the proton is held by the anion of each acid. The resulting salts are liquids, some of which, however, are super-cooled at ordinary temperatures. Several of the salts have been crystallised by moderate cooling.^{1(a)} The crystals have low specific volumes (hardly differing from those of the liquids), and not very sharp melting-points (within about 1-2°). These crystals are obviously of the bulky organic type, each crystal unit containing several molecules, the units being held together by residual valencies or van der Waals forces, and having only low lattice energies. These facts, combined with the low conductivities of the liquids, point either to a high degree of molecular dissociation or to the formation of a high proportion of non-conducting ion-pairs. Reasons have been given for preferring the hypothesis of ion-pairs.

Energy changes involved in the transfer of a proton will be determined as :

- (a) Heats of formation of pure salts unsolvated.
- (b) Heats of formation in the non-ionising solvent, benzene.
- (c) Heats of solution of the salts in water.

Heats of Formation of Salts.

Heats of combination of some acids and anhydro-bases illustrate the principle of proportionality between changes of total and free energy. Thus, aniline and acetic acid, 1.53 Cal.; aniline and sulphuric acid, 8.63 Cal.³; naphthalene picrate, 1.45; quinoline picrate, 13.2; pyridine picrate, 13.84; piperidine picrate, 20.56.⁴ The high heat of formation of the last named salt is associated with high electrolytic conductivity in the fused state. These systems are somewhat similar to those under consideration, but the heats could usually be determined indirectly by the usual process of finding heats of solution of acid, base and salt and the heats of neutralisation of the aqueous solutions. On account of the insolubility of certain picrates, the components had to be mixed in a saturated solution of the picrate in the presence of the solid phase. On account of the insolubility of the higher fatty acids in water an indirect method was precluded in the present work, but a direct method was eminently suitable on account of the nature of the acids, base and salts.

Experimental.

The method employed was to break a bulb containing a known weight of piperidine into an exactly equivalent quantity of the acid contained in an aluminium calorimeter. The rise in temperature of the water in a copper calorimeter surrounding the latter then gave a measure of the heat of the reaction. The specific heat of the salt formed was determined by the method of cooling.

The double calorimeter is shown in Fig. 1. The water equivalent of the apparatus was first determined by the arrangement shown on the right of the Fig. The annular space between the two calorimeters was filled with a known weight of cold water, and about 10 c.c. of water at 75-80° were introduced into the upper vessel. When the temperature in the latter

³ Berthelot, *C.r.*, 1890, 111, 135.

⁴ Vanzetti, *Gazz.*, 1916, 46 (i), 145.

had reached 55-60° (stirring uniformly), the plunger was withdrawn, the warm water fell into the inner calorimeter, the rise in temperature of the water in the outer vessel was determined, and the usual cooling correction was made. The amount of warm water introduced was determined by weighing the inner calorimeter and stirrer before and after the experiment. In this way the conditions of the actual experiment were reproduced as nearly as possible.

The water equivalent of the inner calorimeter, stirrer and thermometer (required for the specific heat determination) was determined by an electrical method. A constantan heating coil was wound round the stirrer, and the temperature rise of about 10 c.c. of water in the calorimeter determined, after passing a current of about 2 amps. at approximately 1 volt for four minutes. The temperature rise was corrected for radiation, and, knowing the electrical work done, the water equivalent could be calculated.

In determining the rise of temperature of the water in the outer calorimeter which resulted from mixing the acid and base in equivalent proportions in the inner vessel, the liquids in the latter were protected from atmospheric moisture by the mercury seal on the stirrer. When steady conditions were obtained the bulb was broken by the stirrer, and, while stirring the liquids in the inner and outer vessels, the temperature rise in the latter was recorded, with the usual correction for radiation.

The specific heat of the salt was found by removing the inner calorimeter, inserting a thermometer in the cork, raising the temperature to 35-40°, and obtaining a cooling curve in a constant temperature enclosure at 0°. By comparing the times required for the temperatures of the salts to fall from 23° to 18° with that taken by an equal volume of water under the same conditions, the specific heats of the salts were calculated, allowance being made of course for the heat capacity of the broken glass.

The accuracy of these experiments depend on the accuracy with which the rise of temperature can be measured. Variations up to 8 per cent. in the specific heats can be tolerated before the 0.5 per cent. accuracy claimed for the final results is affected. This is calculated on the assumption that, after correcting for radiation, the temperature rise is correct to 0.03°. It is more difficult to estimate errors due to the fact that the heat generated in the inner calorimeter may not pass completely into the water in the outer vessel. The errors, however, should be small.

A typical specimen of the results obtained is detailed below; others were calculated similarly, and only the final values are given.

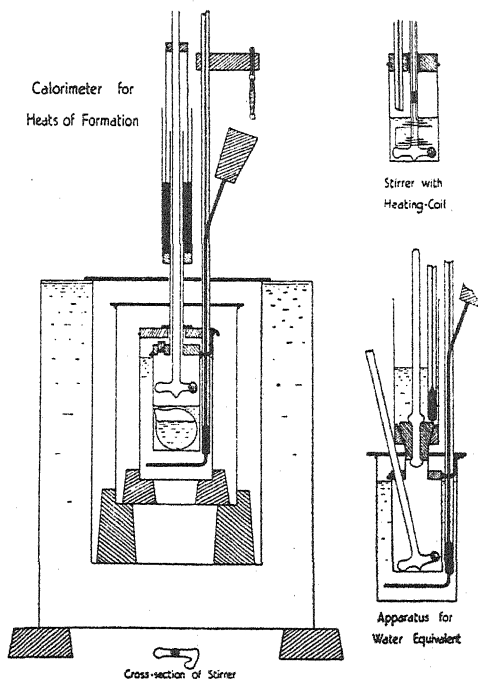


FIG. 1.

Water Equivalent, W, of Double Calorimeter.

$$W = \frac{\text{Mass Hot Water (8.67 g.)} \times \text{fall in temp. (61.4-22.17° C.)}}{\text{Rise in temp. (22.17-16.20° C.)}}$$

Mass Cold Water (42.08 g.)

Hence $W = 14.8$ g. Other determinations confirmed this value.

Water Equivalent, W, of Aluminium (inner) Calorimeter.—Current passed at 0.948 volts through heating coil (calculated water equivalent 0.12) of resistance 0.425 ohms for 243 seconds. Wt. of Water = 9.75 g. Rise of temp. = 6.98°.

Electrical work = Rise of temp. (Wt. of Water + Water equiv. of coil + w),

whence $w = 7.74$ g.

Specific Heats of the Salts.—The data refer to the hexoate of piperidine, cooled from 23° to 18°. C_p , the specific heat of the salt, is then calculated :

$$\frac{\text{Wt. of Water (8.89 g.)} + w}{\text{Time (6.94 mins.)}} = \frac{\text{Wt. of salt (8.10 g.)} \times C_p + \text{water equiv. glass bulb (0.18 g.)} + w}{\text{Time (4.68 mins.)}}$$

The specific heats of the salts from the propionate (C_3) to the octoate (C_8) are as follows :

	C_3	C_4	C_5^*	C_6	C_7	C_8
Specific Heat :	0.42	0.42	0.41	0.41	0.42	0.42

Heats of Mixing Acids and Base.—The data refer to the hexoate :

Wt. of water in outer calorimeter	= 41.5 g.
Water equivalent of glass bulb	= 0.2 g.
Wt. of salt ($C_p = 0.41$)	= 8.097 g.
Rise in temp. during reaction	= 6.16°

The heats of formation per g. mol. thus obtained are :

	C_3	C_4	C_5	C_6	C_7	C_8
Heat of Formation	9.5	9.4 ₅	9.4	9.1 ₅	9.1	8.7 ₅

If the estimate of the accuracy is accepted, these results show a significant decrease in Q with rise of molecular weight of the acid, and, as already shown, this can be explained as due to a decreasing total energy of combination of the proton with acid radicals of higher molecular weight. This can be compared with the decreasing free energy of this combination as shown by the slight diminution in the dissociation constants in water of the higher fatty acids. The parallelism between the conductivity and heats of combination is thus borne out by these salts, which likewise show a decreasing conductivity (and also viscosity-conductivity product) with increasing molecular weight.¹⁰⁾

Heats of Formation in Benzene.

Further information as to the energy of transfer of the proton may be obtained from a study of the reaction in benzene. In this solvent there is no question of varying degrees of dissociation, since the solutions, at the concentration chosen, are non-conductors. Heats of combination of the much weaker base pyridine with acetic acid have already been determined by Mathews⁵ in a number of different solvents and in the pure state. The value for the latter was 2.2861 Cals., as against 2.2746

* *Iso-Valerate.*

⁵ *J. Amer. Chem. Soc.* 1911, **33**, 1291.

Cals. in benzene, which when corrected for the heat of solution of the salt became 2.4817. Such a correction is not applied in the present case, since the object is rather to compare the heats of proton transfer in the absence and presence of solvent.

It was previously shown^{1(a)} by the evidence of temperature coefficient of surface tension that piperidine propionate is associated to a degree of 1.86 between 20° and 30° while in benzene it exists largely as double molecules.^{1(c)} These double molecules in the pure salt are probably, and in benzene solution possibly, ion-pairs of the type postulated by Bjerrum.⁶

Experimental.

The same experimental procedure was adopted in benzene solution as with the pure liquids, except that the outer calorimeter was dispensed with. A bulb containing a 10 per cent. solution of piperidine was broken in an equivalent quantity of a 10 per cent. solution of propionic acid in an aluminium calorimeter (somewhat larger than used in the previous experiments). The rise in temperature was observed. The specific heat of the solution was then found by comparing the rise in temperature obtained when a given current was passed through a heating coil in the solution for a given time with that obtained by the same current for the same time in pure benzene. In this way errors in the specific heat due to evaporation of benzene, and condensation on the upper parts of the vessel, were largely compensated. However throughout the whole experiment every precaution was taken against evaporation or absorption of atmospheric moisture, the stirrer working through a mercury seal.

Results.

Water equivalent of calorimeter, etc.	= 3.6 g.
Wt. of piperidine solution	= 12.56 g.
Wt. of propionic acid solution	= 10.92 g.
Water equivalent of glass bulb	= 0.3 g.
Rise of temperature	= 10.20°
Specific heat of solution	= 0.435

Hence heat of formation of 1 g. mol. of salt in 10 per cent. benzene solution = 9.7 Cals.

It was observed that the temperature rose to a maximum immediately on mixing the solutions. The reaction may therefore be said to be instantaneous and actually took place more rapidly than in the absence of solvent, probably on account of the smaller viscosities of the benzene solutions permitting more rapid mixing. It will be noted that the heat of formation is almost the same as in the solvent-free system, and hence it is probable that the structure of the salt molecule in benzene is very similar to that in the latter condition, *i.e.*, it consists of ion-pairs, in which the proton has passed from the acid to the base. These ions are not, however, free to move, and thus the benzene solution is non-conducting.

Heat of Combination with Excess of Acid and Base.

Preliminary experiments showed that on the addition of further acid to the salt there was a considerable evolution of heat, whereas on the addition of excess of base the heat effect was small. Berthelot³ has investigated a rather similar case in the combination of the considerably weaker anhydro-base aniline with acetic acid. A second equivalent of acid yielded 1.41 Cals.; a second equivalent of base 0.73 Cals. These heats are of the same order as that of the original reaction, 1.53 Cals.

⁶ *Math-phys. Medd.*, 7, 9.

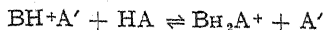
The additional amounts of heat may be due to the formation of an acid or basic salt, but, more probably to the partial reversal of molecular dissociation by the excess of either constituent. It will be noted that excess of acid has the greater effect, no doubt on account of its relatively greater strength compared with the base, when a given quantity of acid will yield a greater proportion of salt than an equal quantity of base.

Experimental.

Piperidine propionate, having the greatest heat of formation, was chosen for this experiment. A weighed amount of the acid was broken in an equivalent weight of the salt, and the temperature rise observed. The specific heat of the resulting mixture was determined by the method of cooling. The operation was then repeated, mixing the base with the salt.

	<i>Excess Acid.</i>	<i>Excess Base.</i>
Total wt. of liquid	7.874 g.	7.454 g.
Water equivalent of bulb	0.13 g.	0.13 g.
Water equivalent of calorimeter, etc.	7.74 g.	7.74 g.
Rise in temperature	14.7°	2.30°
Specific heat	0.35	0.40 ₅
Heat of combination of salt with 1 mol. excess of either constituent	4.82 Cals.	0.79 Cals.

The heat of mixing the base with salt is hardly greater than that which is frequently observed in mixing two chemically indifferent liquids, and there is no reason to suppose that further combination has taken place. On the other hand, the addition of another equivalent of acid gives about half as much heat as that which is evolved in the formation of the salt itself. In studying the physical properties of these mixtures of the lower fatty acids and piperidine, the same difference of behaviour has been noticed throughout. Density-composition curves are linear on the side of excess base, but show large positive deviations on the acid side. Viscosity curves are less steep on the acid side. Molar conductivity curves show a more pronounced maximum on the acid than on the basic side, and, when corrected for viscosity, the only maximum occurs on the acid side. An increased dissociation is therefore found here, and, since the excess acid and base are poor ionising media, it is most natural to suppose that the increase of conductivity and heat is due not to increased electrolytic dissociation of existing ion-pairs but to increased proton addition according to the scheme:



The ions on the right are electrolytically dissociated.

It may be noted that appreciable quantities of heat are evolved when still further excess of acid is added.

Heats of Solution in Water.

Heats of solution of salts containing organic ions are usually not high. Thus sodium propionate⁷ gives 3.05 Cals. piperidine hydrochloride,⁸ — 0.96 Cals. These two solid salts are highly dissociated before and after solution. Pyridine acetate⁵ gives 1.928 Cals. This salt is liquid, and is largely undissociated both in the anhydrous state and in solution. These small heats of solution are therefore due to the hydration of ions or molecules respectively.

⁷ Hassol, *Ann. Chim. Physique*, 1894, 1, 145.

⁸ Colson, *C.R.*, 1890, 14, 266.

Piperidine salts of the lower fatty acids belong to a different category, and give high heats of solution, of the same order as their heats of formation. It has been shown that the salts are probably only slightly dissociated in the anhydrous state. When in aqueous solution, however, they behave as typically strong electrolytes, their degree of dissociation being much the same as those of potassium salts at the same dilutions. Heats of solution must therefore be due to the formation of the piperidinium and fatty acid ions, and, as shown below, the heat of formation of water from its ions is involved.

Experimental.

On dilution of a specimen of piperidinium hexoate to N/10 concentration, a rise of temperature of about 1° was observed, but further dilution gave no appreciable change. Such a solution was therefore taken as "dilute" in the thermochemical sense.

The experiments were carried out in the copper calorimeter shown in Fig. 2. The water equivalent of the apparatus was determined by a method similar to that already described. About 25 c.c. of warm water were introduced into the vessel secured in the cork of the calorimeter, and shown on the right in Fig. 2. The calorimeter contained about 200 g. of cold water, into which the warm water was introduced by withdrawing the plunger. The temperature of the warm water being known, and the rise in temperature of the cold water thus determined by a Beckmann thermometer, the water equivalent of the apparatus could be calculated.

The heats of solution of the salts were determined by introducing these liquids into glass bulbs, securing the latter beneath the stirrer in the manner shown, and then breaking the bulbs in such a weight of water that the resulting concentration was 1 g. mol. salt : 500 g. mol. water. The results tabulated below are given correct to 1 per cent.

Salts of Fatty Acids :	C ₃	C ₄	C ₅ (ins)	C ₆	C ₇	C ₈	
Heats of Solution :	9.4	9.3	10.0	9.3	9.0	8.5	Cals.

These heats are of similar magnitude to the heats of formation, and also decrease with increasing molecular weight of acid. The order is not, however, the same since these values only begin to diminish appreciably at the heptoate, and the iso-valerate has an exceptionally high value. The dilute solutions from the iso-valerate onwards show a slight cloudiness which is probably due to the occurrence of hydrolysis. This effect would

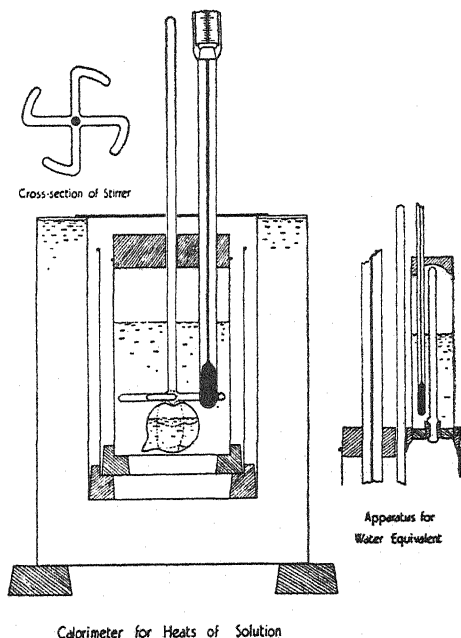


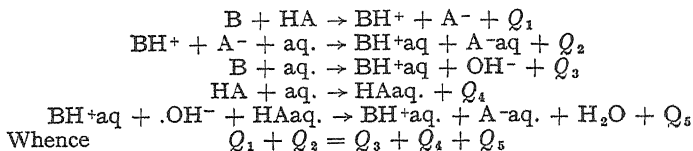
FIG. 2.

naturally not be observed with the propionate and butyrate, whose acids are completely miscible with water.

Heats of Neutralisation.

These heats can be calculated in certain cases from existing data. Heats of neutralisation of the fatty acids from formic to *n* valeric were determined by Berthelot⁹ and similar investigations were made by Massol,¹⁰ who found 12.95 Cals. by KOH and 12.49 Cals. by NaOH. If a mean value of 13.1 Cals. is chosen, the difference between this and the heat of formation of water 13.7 Cals. is - 0.6, which is the heat of ionisation of the propionate ion. The heat of neutralisation of piperidine by HCl¹¹ is 13.01 Cals. or 13.34 Cals.¹² Therefore the heat of dissociation of the small amount of undissociated base is about - 0.6 Cals. Hence the calculated heat of neutralisation of piperidine by propionic acid is (13.7 - 0.6 - 1.0) that is, 12.1 Cals.

This heat which is called Q_5 below will now be calculated by a route which includes the heats of formation and solution tabulated above.



The heat of solution of piperidine¹³ Q_3 is + 6.46 Cals. while that of propionic acid¹⁴ is + 0.62 Cals. Therefore, introducing the values given above for Q_1 and Q_2 , $Q_5 = 11.8$ Cals.

In view of the variability in the older data, and the probable error of our own experiments, this is a satisfactory agreement, and adds confidence to the thermal constants which were the object of the present research.

⁹ *Ann. Chim. Physique*, 1875 (5), 6, 327.

¹⁰ *C.R.*, 1891, 112, 1136.

¹¹ Colson, *C.R.*, 1889, 109, 743.

¹² Berthelot, *C.R.*, 1890, 111, 289.

¹³ Berthelot, *Ann. Chim. Physique*, 1890, 21, 372.

¹⁴ Massol, *ibid.*, 1894, 1, 145.

STUDIES IN ELECTRODE POLARISATION. PART I. THE ACCURATE MEASUREMENT OF THE POTENTIAL OF A POLARISED ELECTRODE.

By A. HICKLING.

Received 22nd October, 1937.

In the investigation of electrolytic processes, a knowledge of the potential of the working electrode is frequently of primary importance. Two methods have been used for measuring such potentials,—the *direct* method and the *commutator* method. In the direct method the working electrode is connected with a standard electrode, and the e.m.f. of the combination measured while the polarising current is flowing. If there is any appreciable resistance between the tip of the tube connecting the standard to the working electrode and the point at which the latter is connected to the potentiometer system, a fall of potential equal to the

product of the resistance and the current strength will be included in the measured potential of the working electrode. Although the idea of a considerable *transfer* resistance at the surface of a polarised electrode is now discredited,¹ there is always present a certain *surface* resistance due to gas evolution and depletion of electrolyte in the diffusion layer, and in the case of an anode the surface may become covered with a poorly conducting oxide film. In view of these factors, potential measurements by the direct method, at any but the most minute currents, may involve a considerable error, *e.g.*, at 0.1 amp. a surface resistance of 10 Ω would lead to an error of 1 volt in the measured potential.² The commutator method was devised to overcome this difficulty; in the method as perfected by Glasstone,³ the almost instantaneous potential of the polarised electrode is measured at chosen fractions of a second after the circuit is broken, and the results so obtained are extrapolated to give the value at zero time, *i.e.*, at the instant of switching off the polarising current. This method, while satisfactory in principle, is in practice attended by a number of difficulties which may be briefly summarised:

- (a) The minimum "off" period which can be conveniently obtained with a mechanical commutator is of the order of 0.001 sec., and this is too long to permit of accurate extrapolation where the rate of electrode potential decay is rapid, as is the case when a good depolariser is present.
- (b) The current reading with the commutator in operation is in general different from that when stationary, and it is therefore doubtful what value is to be assigned to the polarising current.
- (c) It is uncertain to what extent the electrode potential may be affected by induced currents due to repeated "make and break" of the circuit.
- (d) The method is cumbersome, requiring a minimum of four observations for each potential, and involving frequent mechanical adjustment of the commutator. Furthermore, incidental difficulties due to wearing of the contacts, electrical leakage, and variable motor speed, are of frequent occurrence.

The present method was devised to eliminate these difficulties. It utilises an electrical interrupter, free from moving parts, whereby the polarising current can be stopped for any chosen period from 10^{-5} to 20×10^{-5} sec., with any desired frequency, the potential being measured by a special potentiometer which is left in permanent connection with the electrode and designed to measure transient maximum and minimum voltages. In the absence of any effect due to induced currents, the maximum value recorded by the potentiometer should be the same as that obtained by the direct method, as is found to be the case, while the minimum value should be a measure of the potential at the end of the "off" period, and this, when the shortest time interval is utilised, is

¹ For review paper see Denina, *Gazzetta*, 1934, 64, 527.

² Although the possibility of a resistance error has been known for a considerable period, it has been ignored by many workers, and potential values have been published in recent years with an apparent accuracy of 0.001 volt when actually an indeterminate resistance error several hundred times this has been included in the measurements. Many of the impossibly high anode potentials recorded in the literature (*e.g.* 3-4 v. for anodes in aqueous solution) are probably due to this cause.

³ *J. Chem. Soc.*, 1923, 123, 2926; 1924, 125, 250. See also Knobel, *J. Amer. Chem. Soc.*, 1924, 46, 2613; Sand, Grant and Lloyd, *J. Chem. Soc.*, 1927, 378.

found to be practically the same as the true electrode potential, except with the most rapid depolarisation processes. In the latter case measurements with a number of different time intervals, obtained by the simple rotation of a dial, may be made, and extrapolation to zero time carried out. Owing to the shortness of the time intervals, the current readings with the interrupter on and off are not appreciably different.

Experimental.

The Interrupter.—The necessary circuit is shown in Fig. 1, the interrupter embodying the components enclosed by the dotted square.

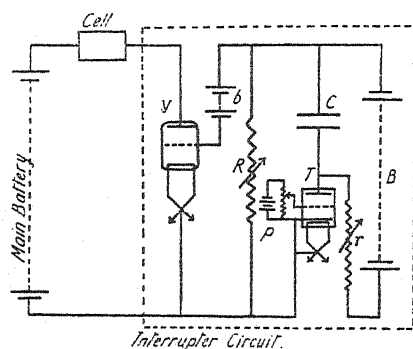


FIG. 1.

of current. As soon as the condenser discharge current drops to a small value, the grid of the valve approaches its initial condition and the main current flows again, the duration of the interruption depending upon the time taken for the condenser voltage to drop by a given amount and therefore being directly proportional to the value of R . When the condenser voltage drops below about 12 volts the thyatron is extinguished, and the process thus repeats itself indefinitely.

In the interrupter constructed, B was a 60 v. dry battery of small capacity (the current taken from it is very small), and C was a $0.5 \mu\text{F}$ condenser. The resistance r , which controls the frequency of interruption, was a $100,000 \Omega$ variable "Clarostat." T was an Osram thyatron, type GT5E, capable of passing a peak current of 5 amps., and its flashing over voltage was adjusted to any desired value by means of the small biasing unit ρ , consisting of a 3 v. dry battery and a $100,000 \Omega$ potentiometer; the heater of the thyatron was driven from a 4 v. transformer. R was a 1000Ω variable resistance of the circular type, equipped with dial. The maximum current which can be interrupted is limited only by the anode current which the valve V can pass. In the present case two Osram PX25 valves were used in parallel, and with a 200 v. main battery, currents up to 0.5 amp. could be used.⁵ The current was changed as desired by varying the input voltage of the transformer supplying the filaments. This method of control was found to be the most satisfactory, as under these conditions, the period of interruption is practically independent of the magnitude of the current passing; b was a small 6 v. dry battery

⁴ For a full account of the construction and properties of the thyatron valve, see Lewer and Dunham, *G. E. C. Journal*, 1932, Nos. 2 and 3.

⁵ There seems no reason why a triode valve capable of passing large currents at low anode voltages should not be constructed; nothing of the kind is at present available as, for wireless purposes, valve research has been mainly directed to the limitation of anode current and the raising of working voltages.

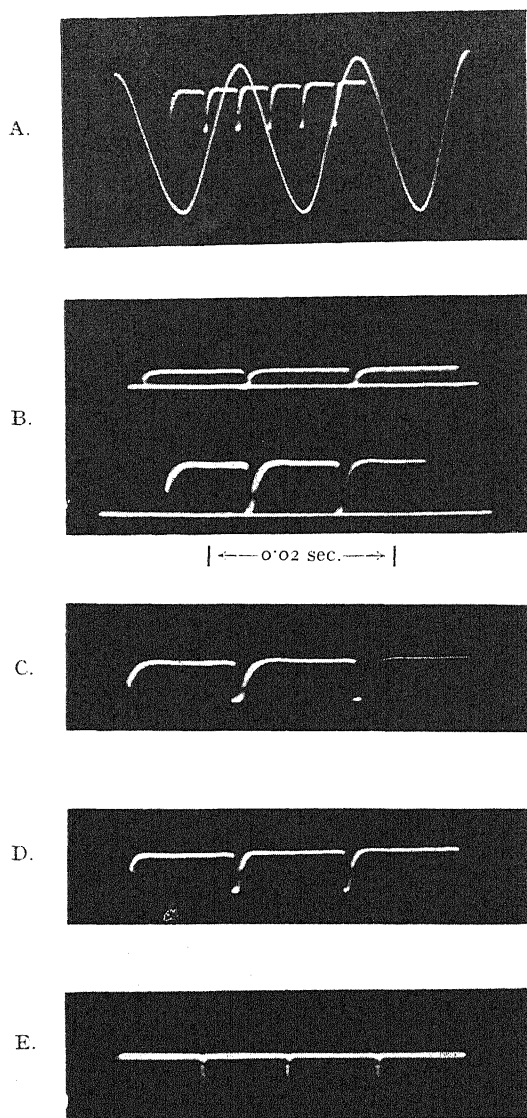


FIG. 2.—Oscillograph Records.

[To face page 1543.]

which served to keep the grids negative under all circumstances. Although not necessary in any way for the functioning of the interrupter, it was found convenient in practice to connect a high resistance telephone across R to give an audible indication when the instrument was working.

The behaviour of the interrupter was investigated by placing a resistance in the main current circuit, and connecting the ends to the deflecting plates of an oscillograph. Some of the results, photographically recorded, are shown in Fig. 2. Photograph A, which gives a general qualitative idea of the action of the interrupter, shows the wave form with the longest time interval operating, superimposed on ordinary 50-cycle alternating current. It is to be noted that the interruption is absolutely sharp; the frequency of interruption is not important for most purposes, but in practice it is convenient to work at about 100 per sec. B, C, D, and E are on an extended time base, as indicated. B shows the interruption for two different currents, superimposed on the undeflected oscillograph track; it is seen that the interrupter reduces the current accurately to zero in each case. C, D, and E show the interruption with R having values of 1000, 500, and 50 Ω severally; the first, the longest time interval, is found by measurement from the photograph, and also by calculation, to be 20×10^{-5} sec., and hence D and E correspond to interruptions of 10×10^{-5} and 10^{-5} sec. respectively. It is probable that interruptions yet briefer than 10^{-5} sec. could be obtained with the apparatus, but it is uncertain if the instrument used for potential measurements (*vide infra*) could respond completely in a time interval much less than this.

The Potentiometer.—For the measurement of the transient maximum and minimum voltages a special potentiometer using a thyatron valve is employed. Its operation depends upon the fact that the thyatron passes no current if the grid is more negative than a certain value, dependent upon the anode potential, and that this critical point is very sharply defined. If the thyatron is adjusted to the

critical point, and then an unknown e.m.f. opposed by an ordinary potentiometer is introduced into the grid circuit, the critical adjustment will be restored when the potentiometer reading is equal to the unknown potential. If the unknown e.m.f. is varying and is connected so as to make the grid of the thyatron more negative than the critical value, then it is apparent that the potentiometer will measure its minimum value, while if it is introduced so as to make the grid more positive, the maximum value will be recorded. For convenience in use it is desirable that the thyatron should be automatically reset several times a second, and that the critical point should be clearly indicated in a simple manner.

The circuit employed is shown in Fig. 3. The condenser C is charged by the battery B through a resistance R , and when it attains a sufficient potential it discharges through the thyatron T , producing a sharp click in the loudspeaker S . The grid circuit of the thyatron includes a resistance r (to limit grid current), a small potentiometer unit p for adjusting the grid potential to the critical value, and switching arrangements S_1 and S_2 , by means of which the unknown potential X and the opposing potentiometer P can be either excluded from the grid circuit or introduced in any order; it is also arranged, as shown, that in opening S_1 or S_2 the anode circuit is broken. In using the instrument, S_2 is first closed and p adjusted until the grid attains the critical potential as indicated by a slow regular ticking from the loudspeaker; on one side of the critical point there is

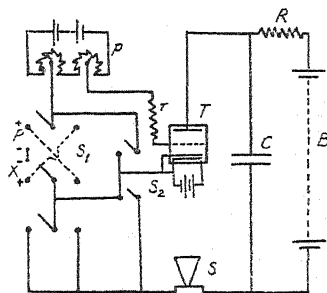


FIG. 3.

silence, and on the other the ticking rapidly becomes a continuous buzzing sound. S_2 is then opened and S_1 closed, and the critical point again found by adjusting the main potentiometer P; according as S_1 is to the left or to the right, the minimum or maximum values of the unknown potential X will be read from the potentiometer. By closing both S_1 and S_2 , the combination of P and X is short-circuited, and if there is a galvanometer in circuit, a measurement of X by the ordinary potentiometer method may be made.

The components used in the circuit had the following values: B, small capacity 30 v. dry battery; R, 5000 Ω ; C, 0.5 μ F; S, low resistance loudspeaker; T, Osram GT1A, the heater being supplied from a 4 v. accumulator; r , 10,000 Ω ; p , 4 v. dry battery with 5000 and 100 Ω wireless potentiometers connected across it series, one serving as a coarse, and the other as a fine control. P was usually a potentiometer-voltmeter reading directly to 0.01 v.; actually the grid of the thyatron is sensitive to changes of potential smaller than this, but in view of the difficulty of reproducing polarisation potentials it is doubtful if measurements supposedly more accurate than 0.01 v. have any significance. The grid current taken by the thyatron in the vicinity of the balance point is of the order of 1 μ a.

The potentiometer was tested by measuring the maximum and minimum values of a combination of a steady voltage and an intermittent voltage obtained by means of the interrupter, and gave completely satisfactory results.⁶

Electrode Potential Measurements.—The examples in Table I. are illustrations of the application of the method to the elimination of the resistance error in potential measurements.

TABLE I.

Current (amp.).	Potential in Volts.							
	Direct.	Maximum.	Minimum.					
			5	10	20	30	45	Extra- polated.
0.01	— 0.65	— 0.65	— 0.64	— 0.63	— 0.62	— 0.60	— 0.57	— 0.65
0.025	— 0.75	— 0.75	— 0.65	— 0.64	— 0.62	— 0.60	— 0.58	— 0.66
0.05	— 0.81	— 0.81	— 0.66	— 0.65	— 0.64	— 0.62	— 0.59	— 0.67
0.10	— 0.94	— 0.94	— 0.66	— 0.65	— 0.64	— 0.62	— 0.58	— 0.67
0.20	— 1.19	— 1.20	— 0.66	— 0.64	— 0.62	— 0.60	— 0.57	— 0.67
0.30	— 1.32	— 1.33	— 0.66	— 0.65	— 0.63	— 0.61	— 0.58	— 0.67

The hydrogen evolution potentials at a smooth platinum cathode, 1 sq. cm. in area, in a 0.1 N-sulphuric acid electrolyte saturated with hydrogen, were measured at a number of different currents by the direct method, and also by the new method. A saturated calomel electrode was used as reference electrode, the electrolyte syphon pressing lightly upon the cathode. The minimum potentials for dial readings on the interrupter of 5, 10, 20, 30 and 45 are recorded, these being directly proportional to the duration of the "off" period, the 45 value corresponding to 20×10^{-6} sec. The maximum potentials were found to be the same for all dial readings, and a single value of each is therefore recorded. The measurements were made at room temperature, about 18°, and are given on the hydrogen scale. The cathode was polarised for 30 min. at 0.2 amp. before observations were made.

⁶ This potentiometer appears capable of extensive application to electrical measurements, and a fuller account of it with constructional details will appear shortly in the *Journal of Scientific Instruments*.

It may be noted that as the current is increased above 0.01 amp., there is a considerable and increasing error in the measurements by the direct method, until at 0.3 amp. the apparent value of the potential is about twice the true value. By the new method it is seen that the maximum values are the same as those obtained by the direct method, but the minimum values are much lower, and indicate that the hydrogen potential is only slightly raised by rise of current. The minimum values for the shortest time interval are within 0.01 v. of the values extrapolated from the series of measurements. As would be expected, moving the syphon of the reference electrode relative to the cathode had a considerable effect on the potential measurements by the direct method, but scarcely changed the minimum values obtained by the new method. This is shown by the following values for a current of 0.1 amp.:—

Distance of syphon from cathode (cm.)	0	1	2	3
Potential by direct method . (v.)	— 0.94	— 1.09	— 1.24	— 1.35
Minimum potential (shortest interval) . . (v.)	— 0.66	— 0.66	— 0.67	— 0.67

Measurements were also made of the oxygen evolution potentials in 0.1 N-sulphuric acid, using the same electrode after it had been pre-polarised at 0.2 amp. for 30 minutes, other conditions being the same as for the hydrogen evolution observations. The results are given in Table II.

TABLE II.

Current (amp.).	Potential in Volts.							
	Direct.	Maximum.	Minimum.					
			5	10	20	30	45	Extrapolated.
0.01	2.02	2.02	2.01	2.01	2.00	2.00	2.00	2.01
0.025	2.05	2.05	2.04	2.04	2.03	2.03	2.02	2.04
0.05	2.11	2.11	2.05	2.05	2.05	2.04	2.04	2.05
0.10	2.17	2.17	2.06	2.06	2.05	2.05	2.04	2.06
0.20	2.31	2.32	2.07	2.06	2.05	2.05	2.04	2.07
0.30	2.37	2.37	2.08	2.07	2.06	2.05	2.04	2.09

Here again it is seen that at the high currents there is a considerable resistance error, although it is not so large as in the previous example. By the new method the minimum potential for the shortest time interval is within 0.01 v. of the extrapolated, *i.e.* the true, potential in all cases.

As an example of the measurement of an electrode potential which decays extremely rapidly, and to which (for this reason) the ordinary commutator method is inapplicable, the following figures for an anode depolarised by sulphur dioxide may be quoted. The platinum anode used above was again employed, with a current of 0.1 amp., in 0.1 N-sulphuric acid through which a rapid stream of sulphur dioxide was passed. The minimum potentials were as follows :

Dial reading . .	5	10	20	30	45	volts.
Minimum potential .	2.25	2.21	2.15	2.12	2.09	

Accurate extrapolation from these figures is readily possible, and gives a value of 2.29 volts.

Summary.

A new method of measuring the potentials of working electrodes is described, by means of which results accurate to 0.01 volt may be obtained free from resistance error. The method is applicable to electrodes the potentials of which decay rapidly, and may be used for studying the rate of fall of potential in such cases.

The author's best thanks are due to Mr. F. L. Attenborough for photographing the oscillograph records, to Mr. J. H. Bruce for many helpful suggestions, to Dr. L. G. H. Huxley for the loan of apparatus, and to Dr. S. Glasstone for encouragement and advice.

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THE PHOTOCHEMISTRY OF ALKYL NITRITES. III.

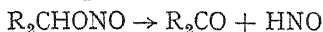
BY H. W. THOMPSON AND F. S. DANTON.

Received 26th July, 1937.

In two previous papers,^{1,2} measurements on the ultra-violet absorption spectra of some alkyl nitrites have been described. A mechanism was suggested for the photo-chemical decomposition of these substances. The earlier spectroscopic measurements were confined to methyl, ethyl, secondary butyl, and *iso*amyl nitrites, all of which have a system of diffuse bands in the near ultra-violet, the intensity distribution within the individual bands being peculiar. The photo-chemical measurements with methyl nitrite and ethyl nitrite suggested as a general mechanism for the primary process of nitrite decomposition,



or



In the present paper the absorption spectra of other nitrites of the series are described, and measurements on the course and products of the photo-decomposition of many of the substances are given, which lead to a deeper understanding of the reaction mechanism.

Attention should be drawn to a paper by Hirschlaff and Norrish* which appeared shortly after the publication of Part II. of the present series, in which these authors postulate a similar mechanism for the photo-chemical decomposition of the related molecules, nitromethane and nitroethane.

Experimental Details.

Methyl nitrite, ethyl nitrite, and secondary butyl nitrite, were prepared as previously described.

n-propyl nitrite, $CH_3CH_2CH_2ONO$, was obtained by the action of nitrous acid upon *n*-propyl alcohol. A cold aqueous solution of sodium

¹ Thompson and Purkis, *Trans. Faraday Soc.*, 1936, **32**, 674.

² *Trans. Faraday Soc.*, 1936, **32**, 1466.

* *J.C.S.*, 1936, 1580.

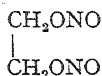
nitrite was added slowly to a well-stirred mixture of *n*-propyl alcohol, with dilute sulphuric acid kept in ice and salt. The upper nitrite layer was separated, washed with cold aqueous sodium carbonate, dried with calcium chloride, and fractionated in vacuo.

Isopropyl nitrite was obtained in a precisely similar manner, but the yield was smaller.

Tertiary butyl nitrite was prepared by the method of Lee and Lynn,³ which depends on the action of nitrosyl chloride upon tertiary butyl alcohol in the presence of pyridine. The nitrosyl chloride vapour (6 g.) was allowed to pass through a trap containing the dried mixture of tertiary butyl alcohol (5 g.) with pyridine (5 g.). The product was a red liquid mixed with solid pyridine hydrochloride. It was washed with ice-cold distilled water, which dissolved unchanged alcohol and the hydrochloride and destroyed the nitrosyl chloride. The green upper layer formed was separated, washed with sodium carbonate and distilled water, dried with anhydrous potassium carbonate, filtered through glass wool and distilled in vacuo.

Cyclohexanyl nitrite was obtained as a yellow oil by the action of nitrous acid upon cyclohexanol in a similar manner to the propyl nitrite. It was washed with a large volume of water to remove unchanged cyclohexanol or cyclohexanone.

Attempts to prepare ethylene dinitrite



by a variety of methods were all unsuccessful. It was found impossible to repeat the procedure given by Bertoni;⁴ the action of cold nitrous acid upon glycol was negligible; and the method of Lee and Lynn using nitrosyl chloride and pyridine, referred to above, gave no result.

The apparatus used in the measurements of vapour pressure was that described earlier by Thompson and Linnett.⁵

The ultra-violet absorption spectra were measured on a Hilger quartz spectrograph E 315. The absorption tubes were glass tubes of varying length, having plane polished quartz ends cemented on.

The apparatus used for the photo-chemical work is shown diagrammatically in Fig. 1.

The nitrite under examination was contained in the bulb A. B was the quartz reaction cell with plane polished ends, and connected to the remainder of the apparatus via the joint C which was sealed with wax. Pressure changes could be followed on the mercury manometer M. The entire apparatus

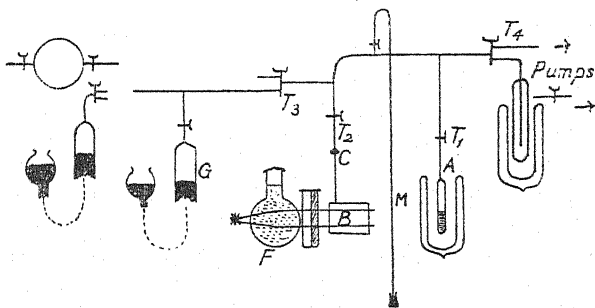


FIG. 1.

could be evacuated through T_4 by a mercury pump backed by an oil pump. The gases in the reaction vessel B could be taken out for analysis into a gas pipette by means of the Toepler device G. The radiation of a

³ *J. Amer. Pharm. Ass.*, 1932, **21**, 125.

⁴ *Gazz. Chim. Ital.*, 1885, **15**, 353.

⁵ *Trans. Faraday Soc.*, 1936, **32**, 681.

mercury arc (running hot) was focussed upon the reaction cell by a spherical quartz flask F containing either distilled water or a filter solution, as described by Bowen.⁶ The ultraviolet triplet at 3655 Å was filtered out by means of copper ammonium sulphate solution in conjunction with Chance's black glass. The temperature in the vicinity of the reaction cell was controlled as far as possible, and minor changes recorded on a thermometer placed alongside the cell.

The gaseous products of a photochemical decomposition were usually examined by the method already described in Part II. As was then explained, the very small quantities of gas available made accurate gas analysis very difficult. For the purpose, however, of forming some qualitative picture of the course of the decompositions, the data obtained are sufficiently accurate. Nitrous oxide (and unchanged nitrite) were dissolved by dilute sulphuric acid or alcohol, unsaturated hydrocarbons by mercuric acetate solution, carbon monoxide by ammoniacal cuprous chloride, and hydrogen and saturated hydrocarbons estimated by combustion in the usual way. Nitrogen remained as a residue. In some cases a simplification could be achieved by separation of the entire gas sample into two fractions by condensation in liquid air.

The residue of a run was lixiviated with water, and the following specific tests for aldehydes, etc., were applied :—

- (i) Schryver's test⁷ for formaldehyde.
- (ii) Linke's test⁸ for paraformaldehyde. The residue was treated with a small quantity of concentrated sulphuric acid and warmed. A glass rod which had been dipped in benzene was held in the vapour. A red colouration indicates the presence of paraformaldehyde.
- (iii) Aldehydes and methyl ketones were detected by the method of Marsh and Fleming-Struthers.⁹ To a small amount of the extracted residue was added a saturated solution of mercuric cyanide in six-normal caustic soda, and the solution was boiled. In the presence of a methyl ketone a white precipitate was formed which settled rapidly, but in the presence of an aldehyde the precipitate darkened and deposited grey metallic mercury.
- (iv) Tests for methyl ketones were also made by the method of Feigl, Zappert and Vasquez,¹⁰ which depends upon their conversion into indigo dyes. A drop of the extract was warmed with a saturated solution of *o*-nitrobenzaldehyde in 2 N caustic soda. On cooling and shaking with chloroform a blue colour is developed. Blank experiments, however, showed that this test is not always reliable.
- (v) Lewin's test¹¹ for acrolein and acetaldehyde was also applied. To the extract solution was added a drop of a saturated solution of sodium nitroprusside, and a drop of piperidine. A blue colour is obtained, which, on addition of ammonia, glacial acetic acid, or hydrogen peroxide, undergoes characteristic colour changes.

In addition to the above tests, derivatives of the aldehydes and ketones, such as the 2.4-dinitro-phenyl hydrazones were prepared and their melting-points determined.

Vapour Pressure Data.

The vapour pressure of each of the alkyl nitrites studied was measured at a series of temperatures. In each case the plot of $\log p$ against $1/T$

⁶ *J.C.S.*, 1932, 2236; 1935, 506.

⁷ See Thorpe and Whiteley, *Organic Analysis*, p. 99.

⁸ *Chem. Zentr.*, 1901, 5 (ii), 130.

¹⁰ *Mikrochem.*, 1935, 17, 165.

⁹ *J.C.S.*, 1905, 1878.

¹¹ *Ber.*, 1899, 32, 3388.

TABLE I.

Substance.	A.	B.	λ_v cal.	λ_v/T_b .	Boiling Point °C.	
					(extrap.).	(record or meas.).
Methyl nitrite	(a) 1098	7.19	5000	19.75	-18	-12 ¹²
	(b) 1095	7.16	4990	19.5	-17	-12
Ethyl nitrite	(c) 1453	7.88	6650	23.1	16.9	17 ¹²
	(d) 1340	7.50	6110	21.1	17	17
<i>n</i> -Propyl nitrite	1480	7.47	6750	21.0	49.0	43-46 ¹³ 57 ¹⁴
<i>Isopropyl</i> nitrite	1360	7.22	6200	19.8	40 ± 1	45/762 mm. ¹⁴ 39/752 mm. ¹⁵
<i>sec.</i> Butyl nitrite	1545	7.33	7036	20.3	73 ± 3	68-9
<i>tert.</i> Butyl nitrite	1610	7.66	7330	21.7	63 ± 1	63

was a fairly satisfactory straight line. Extrapolation of the plot to \log_{10} 760 gave a measure of the B. Pt. and served to check the purity of the sample. In Table I the results are summarised. A and B are defined by the equation

$$\log_{10} p = -A/T + B.$$

$\lambda_v = 2.3 \times RA$ the latent heat of vaporisation; λ_v/T_b is the Trouton Constant (the entropy change at the boiling-point). The actual experimental data are shown graphically in Fig. 2.

The data now given for methyl nitrite (b) are almost identical with those previously given by Thompson and Purkis (a). The data for ethyl nitrite (d), while leading to an accurate boiling-point, do not agree with those (e) of J. W. Goodeve.¹² Since the value obtained from the present measurements for the Trouton constant falls into line with the values

of this quantity for the other compounds in the series, whereas that suggested by Goodeve is anomalous, it seems likely that the present data are the more satisfactory. The extrapolated boiling-points are in general close to those

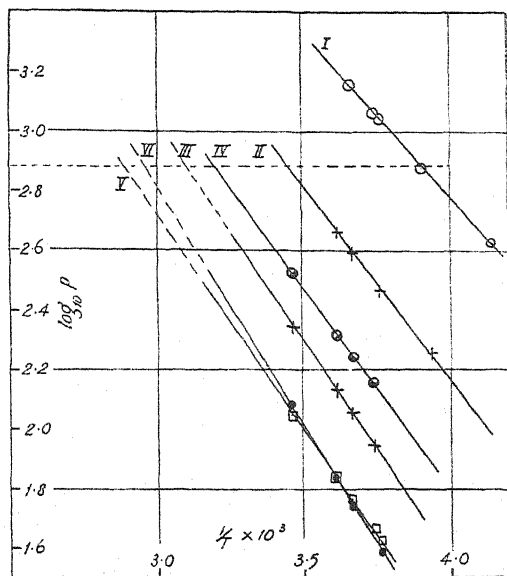


FIG. 2.

- I Methyl nitrite. II Ethyl nitrite.
 III *n*-Propyl nitrite. IV *iso*Propyl nitrite.
 V *sec.* Butyl nitrite. VI *Tertiary* Butyl nitrite.

¹² *Trans. Faraday Soc.*, 1936, **32**, 674; 1934, **30**, 504.

¹³ Cahours, *C.r.*, 1873, **77**, 749.

¹⁴ Silva, *Bull. Soc. Chim.*, **12** (2), 226.

¹⁵ Bewad, *J. Russ. Physik. Chem. Gesell.*, **24**, 125.

determined by other methods, although the values recorded in past literature are in some cases clearly unsatisfactory, *e.g.*, the boiling-point of *n*-propyl nitrite is given as 43-46° or 57° C.

The Absorption Spectra.

All the alkyl nitrites examined show a system of diffuse bands in the near ultraviolet between ca. 3100-4000 Å. At shorter wave-lengths there is a continuous absorption which increases in intensity towards higher frequencies, and with higher pressures of absorbing vapour extends to longer wave-lengths so as to overlap a band system. The distribution of intensity within individual bands is very complex, as described in the cases previously explained in detail. For example, although in general the diffuse bands do not degrade noticeably in either direction, in the case of secondary butyl nitrite there is a distinct degrading to the red. The nature of the bands makes it impossible to give an "accurate" value for the wave-lengths of the band origins, but it is clear that the intervals between successive bands suggest the excitation of a normal vibration frequency of about 900-1000 cm^{-1} . The displacement of the band system towards the red or towards the ultraviolet as the nature of the alkyl group is changed does not appear to follow any obvious rule; minor displacements are noticed, but they are never large.

Photochemical Measurements.

It was suggested, on the basis of the earlier measurements, that the primary process in the photolysis of the alkyl nitrites is the production of an aldehyde or ketone, simultaneous with the liberation of the radical NOH. The subsequent photodecomposition of the aldehyde or ketone undoubtedly led to a complex mixture of products. Some of such secondary photodecompositions could be avoided by the use of a source frequency not absorbed by the aldehydes and ketones. In order, as far as possible, to minimise the secondary complicating processes and to disentangle the various reactions, the photolysis of some of the alkyl nitrites has now been studied in both the full mercury arc and in filtered radiation. Unfortunately, the only suitable frequencies emitted by the mercury arc which are absorbed by the nitrites but might not lead to decomposition of the aldehydes or ketones formed are those of the ultraviolet triplet 3650, 3655 and 3663 Å. This group was therefore used as the filtered radiation.

Table II contains a summary of the products of photolysis detected by the analytical methods described above. A and B refer to experiments in which the full light of the arc and filtered light were used respectively. In the case of the gaseous products P and *p* denote major and minor resultants of reaction.

In (1 A) and (1 B) a white polymer of formaldehyde was deposited. It seems pointless to give the exact proportions in which the products are found, for these depend upon the period of illumination and upon other factors. For these reasons any values which could be given are not very significant. But it is nearly always found that the percentages of nitrogen and nitrous oxide greatly exceed those of hydrocarbons. In the same way the pressure changes not only depend on the nature of the products, but also upon their vapour pressures under different conditions, and it is not possible to give a quantitative correlation of the pressure changes with the course of the reaction in any one case. Actually, when using the full light of the arc a small pressure increase was first observed, but in all cases, except (4 B) and (5 B), the main pressure change was a decrease, amounting in terms of the initial pressure to about 36 per cent. in (1 A) and (1 B), 30 per cent. in (2 A), (2 B), and (4 A), 20 per cent. in (3 A), (3 B), and (5 A), and 35-40 per cent. in (6 A). In (1) and (2) the rate of pressure decrease was fairly regular. In (3) this was not so, but a tem-

TABLE II.

	(1)		(2)		(3)		(4)		(5)		(6)
	CH ₃ ONO.		C ₂ H ₅ ONO.		<i>n</i> -C ₃ H ₇ ONO.		<i>iso</i> -C ₃ H ₇ ONO.		sec. C ₄ H ₉ ONO.		tert. C ₄ H ₉ ONO.
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.
CH ₃ CHO .			yes	yes					yes	yes	
C ₂ H ₅ CHO .					yes	yes					
CH ₃ COCH ₃								yes			
CH ₃ COR .							yes				
HCHO or polymer.	yes	yes			yes	yes	yes				yes
R . COOH .			yes	yes	yes	yes	yes		yes		yes
Acid, not carboxylic								(? HNO ₂) yes		yes	
N ₂ . .	P	P	P	P	P	P	P	P	P	P	P
N ₂ O . .	P	P	P	P	P	P	P	P	P	P	P
CO . .	trace		<i>p</i>		P		P	<i>p</i>	P		P
H ₂ . .	trace										
CH ₄ . .			<i>p</i>				<i>p</i>		<i>p</i>		
C ₂ H ₆ . .					<i>p</i>						P
" Unsatur- ated " perhaps C ₂ H ₄ .					<i>p</i>	<i>p</i>	P	trace	P	trace	trace

porary "arrest" was observed after a 5 to 10 per cent. fall in pressure. Fig. 3 is characteristic of the curves obtained with *n*-propyl nitrite. Clearly several—at least two—independent factors must control the pressure changes. Thus, in addition to the primary photochemical process there will be photolyses of the aldehydic or ketonic products, and also the very complex vapour pressure-temperature relationships of the various substances formed. In (4 A) the pressure changes in the early part of a run were erratic; a mist was simultaneously formed, and drops of liquid were deposited. In (6 A) mist formation was noticed, and crystals were subsequently deposited.

Cases (4 B) and (5 B) differed from the remainder in that a pressure increase, not decrease, was observed. Its magnitude depended on the temperature, and not upon the initial pressure of nitrite, which suggests that the recorded pressures depend on the vapour pressure relations of the products. Droplets of liquid were formed during the run.

Some preliminary experiments were also carried out on the irradiation of tertiary butyl nitrite with the filtered radiation. Prolonged illumination appeared to lead to no pressure change, and all the vapour remaining at the end of a run could be condensed in liquid air. This rather surprising

result suggests that no decomposition occurs under the conditions used, and although the interpretation is not yet clear, the matter needs further examination.

A few experiments were carried out in which a solution of cyclohexanylnitrite in carbon tetrachloride

was irradiated with the full mercury arc. The quartz cell was connected to an inverted U-tube, the open end of which was dipped into mercury. On illumination there was a rapid evolution of gas, the solution became turbid, and a dark deposit was formed. The process appeared complex.

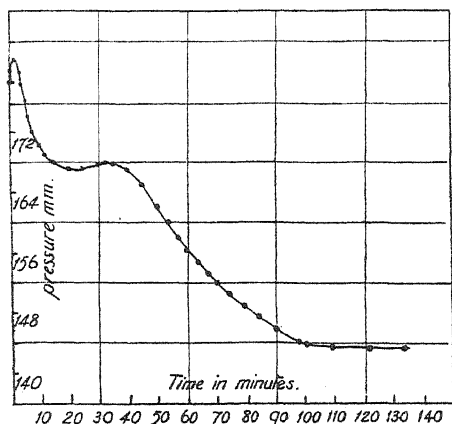
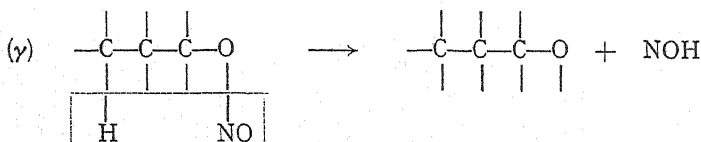
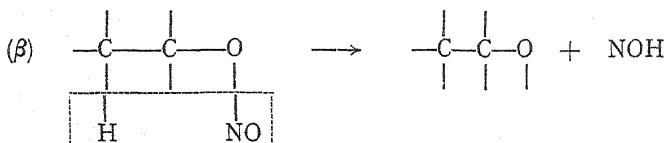
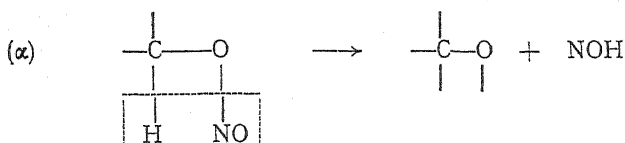


FIG. 3.

Discussion.

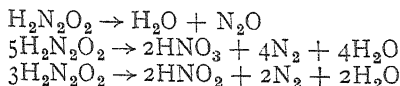
The nature of the spectra—diffuse bands—and the fact that the alkyl nitrites do not show fluorescence in the ultraviolet suggests that

the primary act in light absorption is a dissociation process. All the photochemical data appear to be satisfactorily interpreted by supposing that the NOH radical is split off, together with either an aldehyde or ketone or hydrocarbon (unsaturated) or more than one of these. There appear to be three ways in which the NOH radical may be eliminated, which will be called α , β , and γ , according to whether the H atom of the NOH group comes from the α , β , or γ carbon atom of the nitrite. Thus,



Examples of these types of elimination are discussed for the actual cases below. The secondary processes are apparently numerous, and rather complex. The NOH radicals may associate to form hyponitrous acid, which is known to decompose, giving a mixture of products containing nitrogen, nitrous oxide, and nitrous and nitric acids. Possible

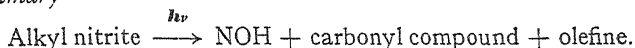
equations suggested by Ray and Ganguli,¹⁶ and by Hantzsch and Kauffmann,¹⁷ are :



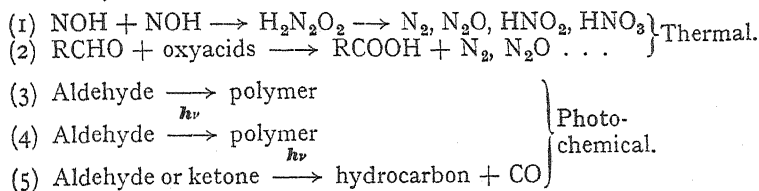
The products of such reactions may oxidise the aldehydes formed in the primary process to give the carboxylic acids found. In fact, whenever an aldehyde was detected among the products, nitrogen oxyacids were not found, but when no aldehyde but a ketone was present, nitrous acid and no carboxylic acid was found. Other secondary processes are also clearly the photolyses of the aldehydes and ketones, which are absent or much less marked in the filtered light. There is also the polymerisation of aldehydes, thermally or photochemically; the polymerisation of formaldehyde will be catalysed by formic acid.

The general scheme of processes will then be of the following form :

Primary

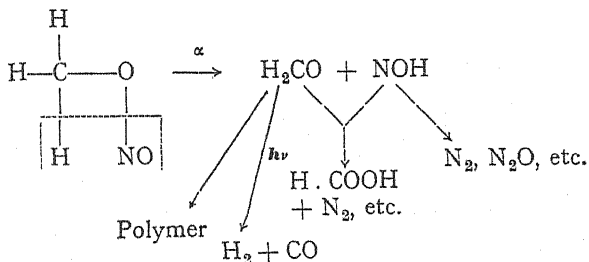


Secondary.

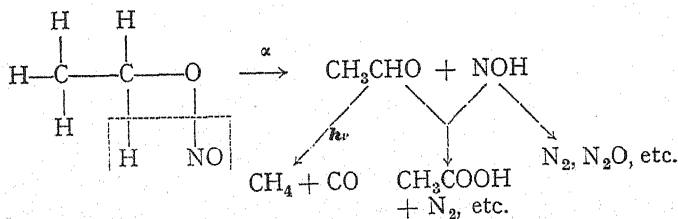


Examples of these changes are shown below.

Methyl nitrite.



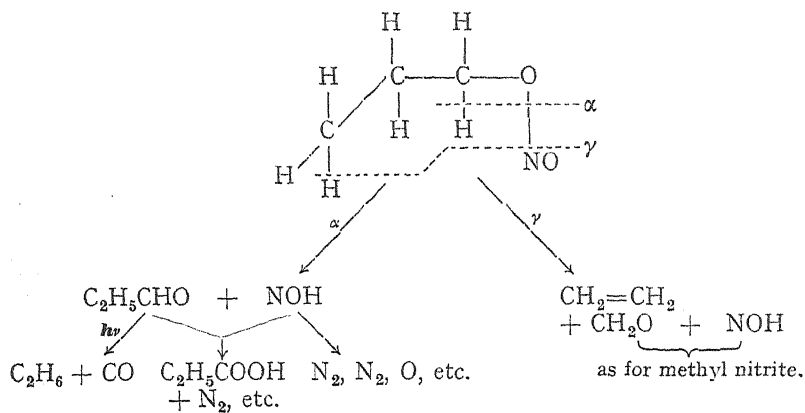
Ethyl nitrite.



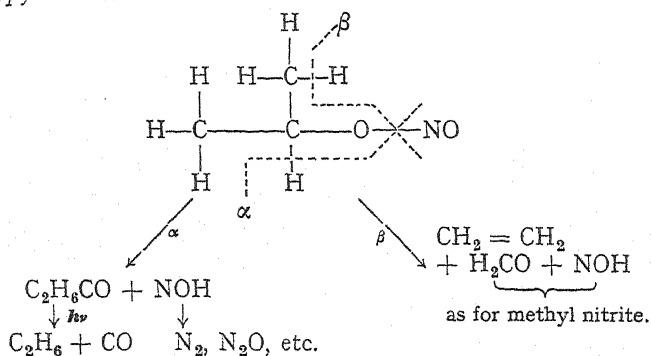
¹⁶ J.C.S., 1907, 1866.

¹⁷ Ann., 1896, 292, 317.

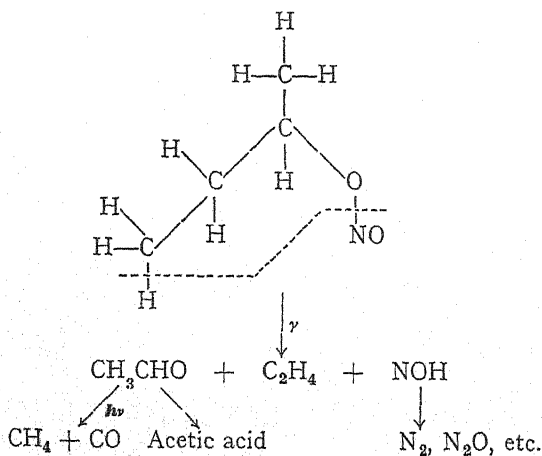
normal-Propyl nitrite.



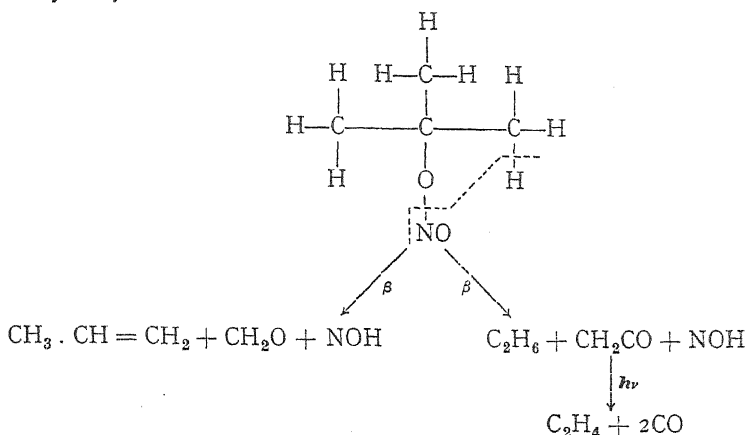
iso-Propyl nitrite.



sec.-Butyl nitrite.



tertiary-Butyl nitrite.



The primary process involved in the above photochemical reactions is an unusual one. Not only is the tendency for the liberation of NOH in itself surprising, but it should also be noticed that while the electronic energy enters the —ONO group, bonds are broken on other parts of the molecule. This indicates the occurrence of some internal redistribution of energy. The relationships are in many ways similar to those found in the photolysis of aldehydes and ketones. It is possible by assuming energy values for the various bonds to estimate the quanta necessary for the various forms of rupture, *i.e.* α , β , or γ . The results do not, however, suggest any reason why one or other type of fission should be particularly preferred. It seems possible that stereochemical considerations play some part in determining this.

It is clear that the conditions which determine the relative probability of the several processes are extremely involved, and further experimental work is essential before they can be completely understood.

Summary.

Earlier work on the spectra and photochemical decomposition of alkyl nitrites has been extended. The products of photochemical decomposition have now been analysed and a mechanism has been suggested to explain the general course of the reactions. This mechanism involves the primary fission of the radical NOH and the formation of aldehydes or ketones, and in some cases of unsaturated hydrocarbons. The secondary processes have also been discussed.

The vapour pressure curves of the alkyl nitrites studied have been measured.

We are grateful to The Chemical Society and to Imperial Chemical Industries Ltd. for grants towards the cost of apparatus.

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A CRITICAL INVESTIGATION AND DEVELOPMENT OF THE "DIFFUSION METHOD" FOR DETERMINING SPEEDS OF ATOMIC REACTIONS.

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(with the partial co-operation of SHINJIRO KODAMA).

Received 5th November, 1937.

PART I.

The "diffusion method" developed by Hartel and Polanyi¹ for the determination of rates of slow atomic reactions is based on the following principle: sodium vapour is introduced through a nozzle at an initial pressure p_T into the gas with which it is to react, and the distance from the nozzle is determined at which the partial pressure of sodium has reached a given value p_0 (i.e., the radius of the "flame"). In the stationary state the following general differential equation holds:—

$$D\Delta p + v \text{ grad } p - K \cdot p \cdot p' = 0 \quad (1)$$

where p is the pressure of sodium, p' that of the reacting gas (halogen), D the diffusion coefficient of sodium from the nozzle, K the velocity constant of the reaction, and v the streaming velocity.

This equation is solved by assuming (1) that v (and hence the middle term) can be neglected; (2) that p' is constant throughout the reaction zone. Geometrical simplifications were also introduced (the spherical diffusion of sodium vapour from the nozzle, etc.). Hartel and Polanyi¹ examined the integrated equation so obtained:—

$$K = \frac{(\ln p_T/p_0 - \ln R/r)^2}{(R-r)^2} \cdot \frac{\delta}{p'} \cdot \frac{1}{T} \quad (2)$$

(where K is the velocity constant, r the radius of the nozzle, and δ the diffusion constant of the sodium vapour in the gas mixture). Apparently this equation was adequately fulfilled. Hartel, Meer and Polanyi,² by more accurate measurements, showed systematic deviations from the relationship between p' and R given by equation (2) and rejected the quantitative use of the method. In the present work the method has been improved and the conditions for obtaining quantitative results have been determined.

1. Apparatus and Method.

(1) **The Circulation Apparatus.**—The apparatus (Fig. 1) consists of a circulation and distillation system. The carrier gas Tr (H_2 or N_2) circulated by the pump P_1 , is introduced into the apparatus at E, and streams in the direction of the arrows $a_2 \rightarrow a \rightarrow a_1 \rightarrow a_2 \rightarrow a_3$. The remainder of the halogen compound which is not removed by reaction in the reaction vessel is condensed in the liquid air traps F_1 and F_2 , and if necessary removed by molten sodium in trap F_3 . The circulation speed

¹ Hartel and Polanyi, *Z. physik. Chem.*, B, 1930, 11, 97.

² Hartel, Meer and Polanyi, *ibid.*, 1932, 19, 139.

of the carrier gas is regulated by a glass membrane valve V_1 constructed by v. Bogdandy, and is measured by the double McLeod M_1 (from the fall in pressure across the capillary K_1 , K_2 or K_3). Two buffer volumes, H_2 and N_2 (each 30 litres, *i.e.*, ten times the volume of the apparatus) serve to prevent fluctuations in pressure in the reaction vessel.

(2) The Distillation Apparatus.—

For reasons discussed later, we also introduced a distillation system which permitted the use of pentane as a carrier gas, and enabled the total pressure to be increased above 10 mm. without any disturbance or fluctuation of the streaming speed. The two systems can be interchanged without interruption of the experiments.

The carrier gas coming from the reservoir C_5H_{12} (V_2 is a metal needle valve for regulation of the streaming speed) flows in the direction of the arrows $a_0 \rightarrow a \rightarrow a_1 \rightarrow b$, through the capillary K_4 and the glass valve V_3 (for the production and regulation of the pressure in the reaction zone) to the liquid air trap F_4 , where it is condensed. The streaming rate is determined from the pressure difference between the manometer Man and the McLeod gauge M_2 . (The McLeod reading gives at the same time the pressure in the reaction vessel.)

The pentane fraction used (boiling-point 29° – 30°) was purified by further distillation in the apparatus by complete removal of the dissolved gases (by using V_2 , P_2 , F_4 , H_2 and H_3).

(3) The Introduction of the Halogen Compound.—The halogen compound HI or HI' , completely air free, enters the reaction vessel at E , through capillary K_5 , K_6 or K_7 . Fine capillaries were used in order to keep the halogen partial pressure as low as possible; (see later, they were so fine that there was considerable inertia in building up the pressure before and behind them). To overcome this in front of the capillaries a buffer volume HI'' was included in the halogen system to diminish fluctuations in pressure, and after the capillaries a by-pass of the carrier gas stream ($1/10$ of the main stream) was caused to flow in the direction E_2 —(or E_3)— E , carrying with it the halogen coming out of the capillary. Frequent calibration of the constancy of the diameter of the fine capillaries was necessary, since even the formation of a film of only 5μ thick in a capillary of radius 0.1 mm. would produce a 19 per cent. decrease in the amount of gas streaming. To effect the calibration, a sample of Tr — HI mixture (sodium being absent) was removed through a long capillary K_8 , running along the interior of the reaction vessel into the adjoining apparatus between taps H_6 and H_7 . From the total pressure and the HI partial pressure (obtained by freezing out HI in F_5 , pumping off the Tr gas, and re-evaporation of HI) and further data, we obtained the value of η_{HI} for a definite pressure difference, thus obtaining a very sensitive indirect check on the constancy of the capillary radius.

(4) Introduction of the Sodium Vapour.—To obtain a pure sodium surface, the metal was freed from hydrocarbons, Na_2O , and Na_2CO_3 by

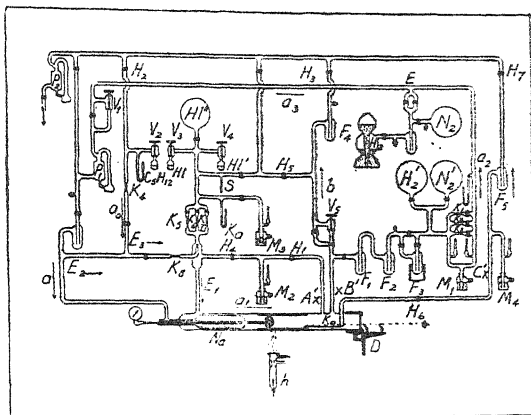


FIG. 1.

several distillations in high vacuum. Before an experiment the oven was heated to a temperature 30° to 50° higher than that used in the experiments (270° C.) in order to avoid delay in building up the pressure due to a surface film, and in attaining the adsorption equilibrium of the carrier gas on the sodium surface as it exists at the experimental temperature. Special experiments showed that, if these precautions are neglected, p_T varies and the reproducibility of the experiments is lowered to 50 per cent.

(5) **Increase of the Intensity of the Sodium Resonance Lamp.**—A self-reversal of the D-line was prevented, by changes in the sodium vapour lamp, and, at the same time, the intensity of emission was increased so that a sodium pressure of even 10^{-6} mm. could be observed. The emission of a continuum, through traces of foreign gases, was suppressed by baking out the electrodes in the arc, and by the use of rigorously purified sodium. The lamp, surrounded by an electric oven of constant temperature, provided sodium light which remained of constant intensity for months, as was shown by the reproducibility of the velocity constants. The special conditions are: 240 volts, 0.1 amp. 2-3 mm. Argon, 100° - 110° C.

(6) **Measurement of Flame.**—The flame was measured by the device D, mounted on the end of the reaction tube, which was closed by a plane parallel glass plate. The upper and lower edges of the flame were observed in line with two thin threads of different colour, which were dimly illuminated, and could be moved vertically by a micrometer screw. The error in measurement was 4 per cent. in the most unfavourable case, corresponding to an uncertainty in the velocity constants of ± 2 to 3 per cent.

Absorption or scattering of light by the deposit on the reaction vessel was avoided by placing in the reaction vessel a glass cylinder, to the end of which a semicircle of iron enclosed in glass was fixed, so that the cylinder could be moved by an external electro-magnet. In this way an uncoated surface could be obtained between the reaction zone and the lamp and frequent cleaning of the reaction tube was unnecessary.

The "blinding" effect of the relatively intense resonance at the centre of the flame (10^{-3} mm. sodium pressure) makes the limiting intensity of 10^{-6} mm. imperceptible. We found rather that a pressure of 10^{-6} mm. corresponds to the actual concentration of sodium vapour on the visible edge of the flame. This is the value chosen for p_0 .

(7) **Total Error in Velocity Constants Obtained by the New Method (in so far as they are of a Purely Technical Nature).**—The reproducibility of the measurements has been improved to 15 per cent. in unfavourable cases, as shown by a large series of analogous measurements taken at different times (over months and years). It is only in the determination of the flame size that the unknown error has technical significance. With a flame of 4 cm. diameter an error of ± 3 mm. would produce a systematic error or ± 50 per cent. in the velocity constants, but the error seldom exceeds 25 to 30 per cent. Finally, the extinction of the sodium resonance by the carrier gas need not be considered as a source of error in the pressure region used.

2. The Partial Pressure of the Halogen Compound before its entry into the Reaction Zone.

The rate of streaming of the halogen compound (n_{HI}) calculated from the pressure fall Δp across the capillaries by application of Poiseuille's Law was found to be inaccurate. The increase of n_{HI} with Δp was far less than was to be expected and, if Δp was kept constant, n_{HI} altered with the mean pressure \bar{p} . Hartel, Meer and Polanyi,² by a somewhat different method, confirmed our results. This source of error causes a perceptible "drift" in the velocity constants with the size of the flame and with the total pressure. We therefore calculated n_{HI} from calibration experiments, using the same method as that used as a check of the capillary radius (sec. 1 (3)). It is, however, necessary to avoid a "diffusion error"

due to the fact that the quantitative composition of the gas mixture in the reaction vessel is not necessarily the same as that of the sample of gas mixture sucked into the adjoining apparatus. As a result of two hundred calibrations, we find that the calibrations are perfectly correct only if they are carried out exclusively with a heavy carrier gas (N_2) and for a \bar{p}' of not less than 3 mm. ($\bar{p}' = \frac{1}{2}(p_{\text{reaction vessel}} + p'_{\text{adj. apparatus}})$) and for a $\Delta p'$ of not less than 2.5 mm. ($\Delta \bar{p}' = (p_{\text{reaction vessel}} - p_{\text{adj. apparatus}})$).

We cannot, therefore, explain the dependence of k upon \bar{p} and Δp by turbulence in the halogen capillaries. In fact, the highest streaming speed used in the halogen and carrier gas capillaries was still less than half the critical speed which is given by the Reynold's number 2000 (relative to the diameter of the capillaries). (Since only very short capillaries with conical ends were used, the Reynold's number is in our case even greater.)

The inapplicability of Poiseuille's Law is due rather to the existence of slip in the gas streaming across the capillaries. In Fig. 2 the shape of

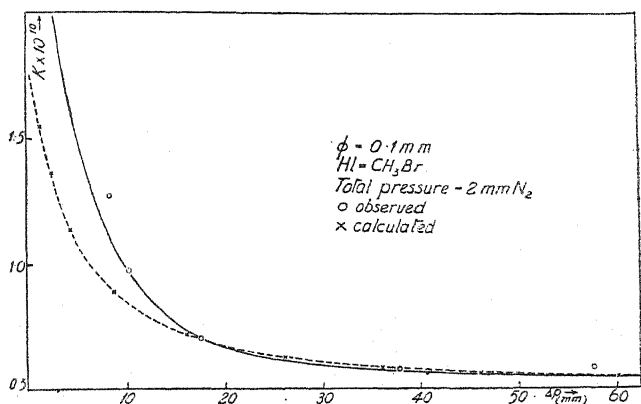


FIG. 2.

an experimental calibration curve is compared with a corresponding theoretical curve on the assumption of a coefficient of slip of $\zeta = 100 \times 10^{-7}$. The ordinates show the "capillary constant"

$$k = \frac{\pi r^4}{8 \eta l^2 R T}$$

The theoretical curve is based on a value of k of 0.454×10^{-10} (p in mm.), obtained from calibrations on the assumption that ζ is $100 \cdot 10^{-7}$. Fig. 2 shows that the character of the calibration curves is satisfactorily explained by the slip. The larger discrepancy at small Δp values is due to uncertainty in the experimental determination of the amount of HI streaming if it becomes smaller than 1/1000 mm.

In the relatively wide carrier gas capillaries, also, the influence of slip, though naturally much less, must not be neglected when \bar{p} is smaller than 2 mm. For instance $\bar{p} = 1$ mm. the slip correction for the widest capillary (3.3 mm. diameter) amounts to 18.5 per cent. (For the smallest halogen capillary of diameter 0.1 mm. the deviation obtained for the same \bar{p} would be greater than 500 per cent.) This correction eliminates the apparent pressure dependence of the reaction velocity.

The most important result of these experiments, however, is that these calibrations are no longer necessary to obtain the true p_{HI} . It can be calculated by the formula:—

$$n_{HI} = \frac{1}{8} \frac{\pi r^4}{\eta l} \cdot \frac{1}{2 R T} \cdot (p_1^2 - p_2^2) \left(\frac{1 + 4\zeta \cdot 2 \cdot 760}{\pi(p_1 + p_2)} \right),$$

in which the only uncertainty is ζ for halogen-glass. From theoretical considerations, however, the true value must lie between 70 and 100×10^{-7} , involving a maximum error in the calibration of η_{HI} of 10 per cent. Thus,

TABLE I.

Substance.	$\eta \times 10^7$ (20°).	$\eta \times 10^7$ (20°) (Landolt-Bornstein).
CH_3Br .	1485	1327
CH_3Cl .	1106	1061
CH_2Cl_2 .	1156	991
CCl_4 .	1177	1000
SiCl_4 .	1144	—
$\text{C}_2\text{H}_5\text{Cl}$.	1050	1050
$\text{C}_3\text{H}_7\text{Cl}$.	1071	—

to replace the tedious calibrations we must, however, know the exact values of η for the halogen compounds used. Table I shows the results of some determinations of η for the principal substances we shall examine. The relative values obtained were converted into absolute values by using the well-known value of η for $\text{C}_2\text{H}_5\text{Cl}$ as reference. For simple halogen compounds we can use a mean value so far as the halogen atoms are the same, but not when they are different; moreover, there is a noticeable increase in viscosity with the number of substituted halogen atoms.

3. The Concentration Distribution of Halogen Compound in the Reaction Zone.

The assumption in equation (1) that the gas reacting with the sodium vapour has a zero partial pressure inside the nozzle but the constant partial pressure p' in the reaction zone cannot be exactly true. We have sought to establish how far this condition is actually fulfilled, and to discover the streaming conditions for which we can assume constant concentration distribution of the reaction gas in the reaction zone, and the minimum back diffusion into the nozzle.

1. **The Method.**—A stream of sodium-free carrier gas and of reaction gas ($\text{C}_2\text{H}_5\text{Cl}$ or $\text{C}_2\text{H}_4\text{Cl}_2$) was introduced into the reaction vessel in concentrations corresponding generally to those used in velocity measurements. Samples of the gas mixture formed in this way were removed through fine capillaries and the concentration of the reaction gas in these samples was determined as previously described (sec. 1). The "diffusion error" (sec. 2) was avoided by using a high streaming speed of the gas in the suction capillaries. The ends of the capillaries (which could be moved by turning a ground glass joint) were so arranged, that from a series of sample analyses the concentration distribution in the reaction zone could be determined (Fig. 3). The samples of gas removed were small, so as not to disturb the concentration distribution in the reaction zone.

2. **The Halogen Distribution Directly in front of the Nozzle in a Plane Normal to its Axis.**—Examining the distribution in a circular plane normal to the nozzle axis, whose centre is about 2 mm. from the nozzle mouth, it was found that p_{HI} decreases on approaching the axis. This decrease was not gradual, a fairly rapid drop in p_{HI} occurring at about 15 to 10 mm. from the edge of the nozzle, as appears from Table II (d_r (in mm.) is the distance normal to the nozzle axis). Furthermore, this "HI impoverishment" increases (p constant)

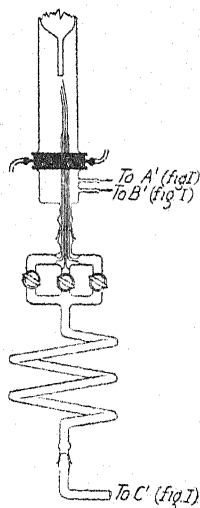


FIG. 3.

TABLE II.—HALOGEN IMPOVERISHMENT IN FRONT OF THE NOZZLE.

(Ethyl Chloride in H_2 . Experiments Nos. 67-73. Temp. 270° C.)

Total p , mm. Hg.	u_{H_2} , mol./sec. $\times 10^3$.	\bar{v} , m./sec.	δ , Na/ H_2 .	v/δ , $\times 10^2$.	d_r , mm.	p_{H_1} , mm. Hg.	Hl Distribn.	Hl Im- poverishment $d_1 \approx 2$ mm.
5.17	12,600		349		2.0	0.071	40.6	
5.03	11,600		359		3.9	0.103	58.8	
4.97	11,600		363		7.8	0.139	79.5	
4.94	10,600	40.8	366	11.37	11.6	0.158	90.2	59.4
4.93	10,800		366		15.4	0.171	97.8	
4.90	10,800		369		19.1	0.166	95.0	
4.91	11,300		368		22.5	0.175	100.0	

with the linear streaming speed v in the nozzle (Fig. 4), and increases with p (v const.). Thus the increase of p and v retard penetration of halogen towards the axis. Since a diffusion process is involved, the halogen impoverishment is, under similar conditions, obviously greater when N_2 instead of H_2 is used (Fig. 7).

We can express these phenomena by the equation:—

$$\frac{p_R}{p_R - p_z} = k \cdot \frac{\delta}{v} \quad (3)$$

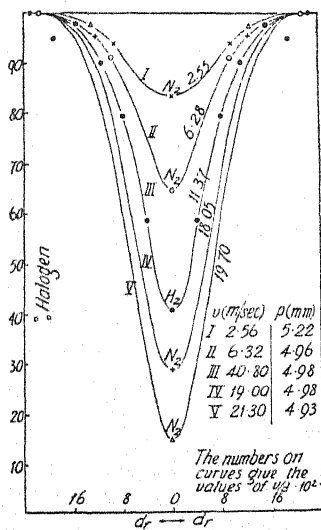


FIG. 4.

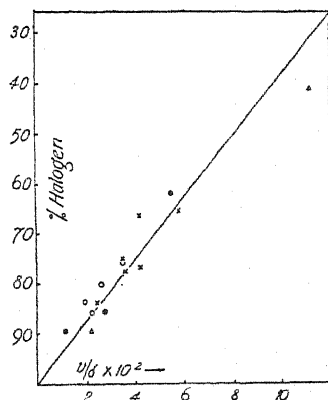


FIG. 5.

Ethyl Chloride:—

X: with N_2 ; without Na range of pressure: 2.04–9.70 mm.

●: with N_2 ; with Na range of pressure: 2.14–2.34 mm.

○: with H_2 ; without Na range of pressure: 4.80–9.82 mm.

Ethylene Chloride:—

Δ: with H_2 ; without Na range of pressure: 1.98–5.17 mm.

where p_R is the value of p_{H_1} on the edge of the flame where the "Hl impoverishment" is zero. p_z that at the place of greatest "halogen impoverishment." δ is the diffusion coefficient of sodium vapour in the carrier gas, and is used as a measure of the alteration of δ' (the diffusion

coefficient of Hl in the carrier gas) with the total pressure and the type of carrier gas.*

The results shown in Fig. 5 confirm equation (3). The experiments include a variation of v between 2 and 40 m/sec. of p between 2 and 10 mm., the use of hydrogen and nitrogen as carrier gas, and C_2H_5Cl and $C_2H_4Cl_2$ as halogen. Since equation (3) is valid for this last variation it is clear that, to a first approximation, the nature of the halogen can be neglected. There is an upper limit to v/δ of approximately 15×10^{-2} , for equation (3) to be valid, corresponding to a limiting halogen impoverishment of about 90 per cent. Above this value the halogen impoverishment decreases instead of increasing with increasing v/δ (for $v/\delta = 16.5 \times 10^{-2}$ the impoverishment should be 100 per cent., but actually it is smaller than 90 per cent., and for 18×10^{-2} it is nearly 75 per cent.), possibly due to the formation of whirls.†

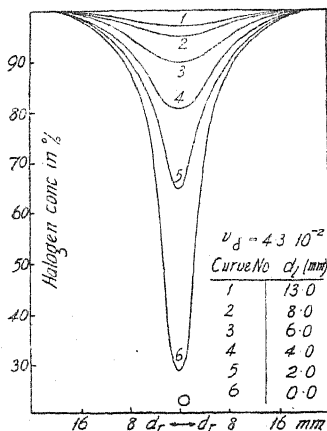


FIG. 6.

3. The Halogen Distribution in Different Planes Normal to the Nozzle

Axis.—Moving along a straight line l in the direction of the nozzle axis, we find a rapid decrease of the halogen impoverishment. This is seen from Fig. 6, where the halogen distribution is given for five circular planes

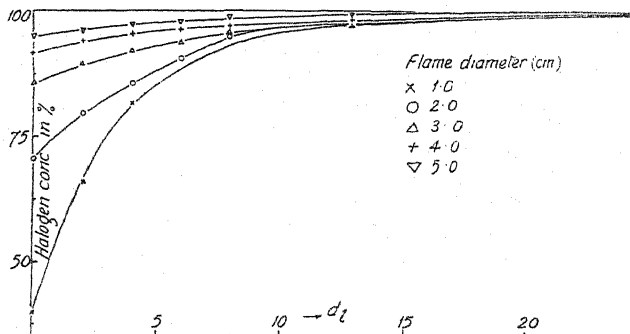


Fig. 7.—Variation with d_2 of the halogen conc. in different cross-sections of the flame hemisphere perpendicular to the axis of the nozzle (for different size of flames).

normal to this line. The distance d_1 of these planes from the nozzle mouth is equally graduated, and the v/δ value is 4.3×10^{-2} ($p = 5$ mm. : $v = 4.6$ m/sec.). N_2 was used as carrier gas.

* We use δ instead of δ' since the value of the latter is unknown. This has also practical advantages. It is assumed that the relative variation of δ and δ' with the total pressure and the type of carrier gas is constant and that under our experimental conditions the mixture ratio does not influence δ' .

† The whirls cannot occur in the nozzle. For streaming in the nozzle the critical v/δ value would be 800×10^{-2} (270°). The whirls occur in front of the nozzle, where there are two streams of different speed side by side (for a central streaming speed of the Na—Tr gas mixture of 40 m/sec. for instance we calculate an outside streaming velocity of the Hal., Tr gas mixture of 1.4×10^{-5} m/sec.). The mixing of these two streams directly in front of the nozzle will lead to whirl formation on hydrodynamic principles.

Considering the different values of the HI-concentration along a cross-section, we obtain the mean halogen concentration in different cross-sections of the flame hemisphere, of which the centre is the nozzle mouth. These calculated results are given for different sphere radii in Figs. 7 and 8 ($v/\delta = 4.3 \times 10^{-2}$). We see from Fig. 7 that by decreasing the flame radius below 3 cm. the spacial inhomogeneity of p_{HI} increases rapidly.

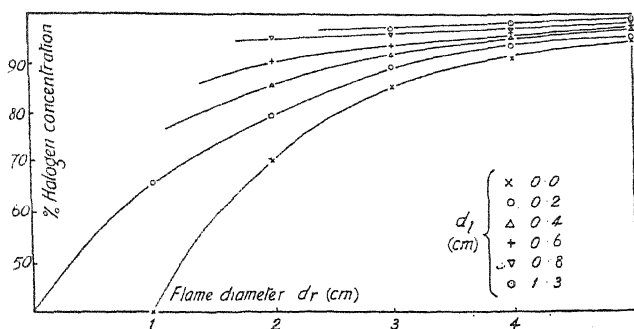


FIG. 8.—Variation with the size of the flame of the average halogen conc. in different cross-sections of the flame hemisphere perpendicular to the axis of the nozzle (for different values of d_l).

4. The Average Halogen Distribution in the Hemisphere in front, of the Nozzle for Flames of Different Diameters.—The average halogen concentration in the total flame space before the nozzle was obtained by integration of six different cross-sectional concentrations. The results are given in Fig. 9 for various flame radii and a constant v/δ value of 4.3×10^{-2} . For this value, in spite of the pronounced halogen im-

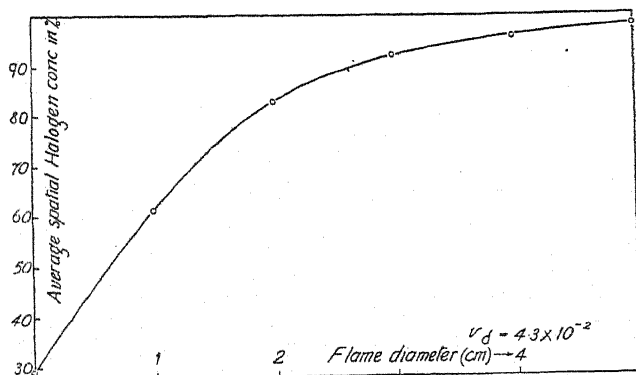


FIG. 9.—Mean halogen conc. in the flame hemisphere in front of the nozzle.

poverishment near the nozzle, the halogen distribution in the total space for large flames approximates to the conditions assumed in equation (1). This value, however, as we will show later (sec. 4), is approximately the lower limit below which the back diffusion of the HI into the nozzle introduces an increasing error of another nature. It is therefore important to know to what extent equation (1) holds if v/δ increases, and approaches the upper limiting value of approximately 15×10^{-2} . For want of experimental evidence we made an indirect calculation on the justifiable

assumption that equation (3), found to be valid for a single point in space, holds also for a collection of points in space:—

$$\frac{p_R}{p_R - p_n} = k_n \frac{\delta}{v} \quad (3a)$$

Where $k_n = f(d_r, d_i)$. In this way we can determine the change of HI impoverishment with increasing v/δ along the axis of the hemisphere (Fig. 10). The value of $k_n = f(d_i)$ results from the fact that by undisturbed

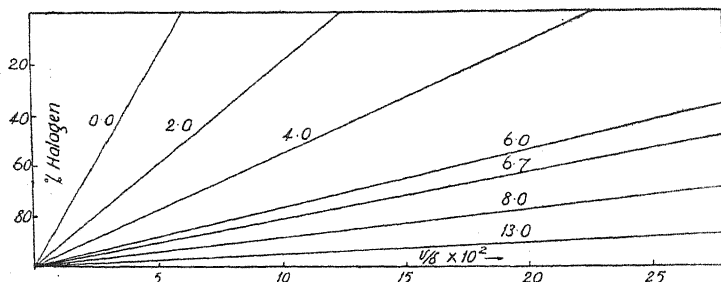


FIG. 10.—Change in halogen impoverishment (with d_r) with v/δ for different d_i . Numbers on curve give values of d_i .

diffusion ($v = 0$) equation (3a) becomes for all points in space:—

$$\frac{p_R}{p_R - p_n} = 0.$$

and that the HI distribution along the hemisphere axis is known for $v/\delta = 4.3 \times 10^{-2}$. Further, we determined by integration the mean halogen concentration in the axis of the flame hemisphere, and used this as a measure of the mean halogen concentration in the total hemisphere. With this simplification, the homogeneity of all distributions appears to

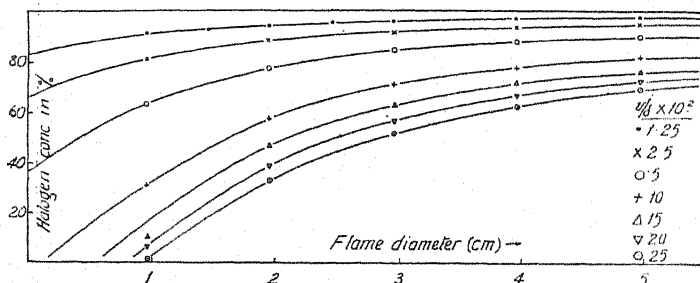


FIG. 11.—Dependence of halogen conc. along the axis of the flame hemisphere on the size of the sphere for different v/δ values.

be worse than it actually is, and we may assume that, for all practical considerations, equation (3a) is valid. Figs. 11 and 12 contain the results. (The relationship for $v/\delta > 15 \times 10^{-2}$ is actually more favourable on account of whirl formation.)

The exact calculation of the aerodynamical relationship in the flame for various values of v/δ , which is of great theoretical interest, involves consideration of $k_n = f(d_r)$. This function can be deduced in all particular cases from the general nature of the curves given in Fig. 6. Table III shows the results of the exact and of the simplified calculation for one v/δ value.

TABLE III.—COMPARISON OF THE EXACT AND APPROXIMATE CALCULATION OF THE HI DISTRIBUTION IN THE WHOLE FLAME.

$v/\delta = 4.3 \times 10^{-2}$.				
Diameter of flame in cm.	2.0	3.0	4.0	5.0
Average HI conc. in per cent. in the flame hemisphere	82.3	91.8	95.4	97.8
Average HI conc. in per cent. along the axis of the flame hemisphere	80.2	86.2	89.3	91.3

5. The Validity of the Results in the Presence of Other Streaming Gases and of Sodium Vapour.—The stationary spacial condition in the flame hemisphere in front of the nozzle is given by the differential equation :—

$$\Delta p - \frac{\omega}{D} \text{grad } p = 0 \quad (4)$$

which obviously bears a direct relationship with equation (3), which refers to the stationary appearance at a point in the space. Undoubtedly, also, one may assume that the ratio of the velocities, *i.e.*, $\omega(x, y, z)$, is constant, so the stationary spacial condition for any carrier gas is the same, if v/δ is the same.

The presence of sodium (Fig. 5), the partial pressure of which was never greater than 10^{-3} , is without any influence on the diffusion of halogen into the streaming gas.

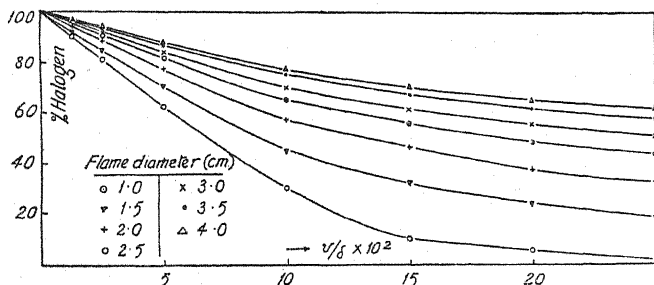


FIG. 12.—Dependence of halogen conc. along the axis of the flame hemisphere on v/δ for different sizes of spheres.

6. The Practical Application of the Results.—The results, especially those of Figs. 9, 11 and 12, lead to a series of important conclusions :—

(a) For flames greater than 3.5 cm. diameter, and for values of v/δ up to approximately 10×10^{-2} , the deviations of the actual conditions from those assumed in equation (1) appear to be permissible, and the systematic change of the deviations with the size of the flame and v/δ is then only relatively small. Thus, the flame sizes to be used experimentally have a lower limit and the v/δ values an upper limit.

An upper limit of the flame size is reached at about 5.5 cms. Larger flames have too diffuse an edge for exact measurement. A lower limiting value of v/δ is necessary to prevent the back diffusion of halogen into the nozzle (sec. 4) ; we shall see later (sec. 4) that this is 5.5×10^{-2} . Thus, using the whole permissible range of v/δ and R variations, the maximum variation in the mean spacial halogen impoverishment is between 23 per cent. and 9.5 per cent.

As explained later, this large range of R and v/δ variation cannot be allowed in the case of very fast or very slow reactions, or when H_2 is used as carrier gas. In all other cases, however, one can obtain exact values

for the *relative* reaction velocity constant K by working under any experimental conditions within the allowed region.

(b) The *absolute* values of K can be approximately determined from those obtained for the largest possible flames and the smallest possible v/δ values (*i.e.*, the optimum experimental conditions) by extrapolation to the ideal condition, $v/\delta = 0$. As to the difference between these two values we conclude experimentally* that, even if the halogen impoverishment is not taken into account in the p_{HI} value used for the calculation of the experimental K , the difference cannot exceed 50 per cent. (in the most favourable part of the allowed experimental range) if the reactions considered have a mean inertia. By introduction of the true mean p_{HI} and by consideration of the p_r -error produced by back diffusion of the HI into the nozzle (sec. 5), this deviation can be reduced to 20 to 30 per cent. This deviation is mainly due to the fact that under the best experimental conditions the assumptions involved in equation (1) cannot be completely fulfilled. The most important part, therefore, of the error in the K values obtained experimentally with the improved diffusion method is due to the uncertainty of the true flame size (sec. 1).† These two errors give the possible difference between the best experimental and the absolute values of K . It is scarcely greater than 100 per cent.

(c) The reliability of the diffusion flame method has been greatly increased since the main systematic variations with experimental conditions (the cause and degree of which were previously largely incomprehensible) were found to be a necessary consequence of the aerodynamic relationships in the flame.‡ These conclusions are completely confirmed by the results of experiments.§

* To be published shortly.

† This error could be reduced by comparing the size of the flame measured visually, and the size as determined photographically. From the latter, using the photometric method of Frommer and Polanyi (*Trans. Faraday Soc.*, 1934, 30, 519), the true value of the sodium pressure on the edge of the visually observed flame could be easily determined.

‡ These are:—

(1) For flame diameters of less than 3 cm. and especially below 2 cm. large variations of K must occur with variation in flame size as well as with variation in v/δ . This appearance of an almost unlimited drift of K at small flame radii, which was already known from earlier experiments, no longer invalidates the use of the diffusion method, since it occurs under conditions which are not in accordance with equation (1).

(2) Above the v/δ value of $\approx 10 \times 10^{-2}$ (later experiments allow this limit to be extended to 12×10^{-2}) the variation in K with v/δ can be expected to be small since here (Fig. 12) the variation of the halogen impoverishment with variation in v/δ becomes insignificant. The absolute extent, however, of the halogen impoverishment is in this region too great to justify an approximate application of equation (1).

(3) Above the purely aerodynamical critical v/δ value of 15×10^{-2} (sec. 3) the reaction velocities may be expected to become still less variable since, as a result of whirl formation, a more uniform halogen distribution occurs, and thus not only the drift of K with v/δ but also the drift with flame size disappears. In this region, therefore, K becomes practically independent of the experimental conditions. These conditions are unfavourable for exact experiments since the assumption of the spherical nature of the flame is no longer exact.

(4) In the region of the permissible v/δ and R variation, the neglect of the effect of halogen impoverishment in the calculation of p_{HI} must produce two kinds of apparent variation of K with experimental conditions. Firstly, there will occur a systematic drift of K with flame size (v/δ remaining constant). The reaction velocity becomes too small with small flames (see Fig. 11). For the limits of $v/\delta = 5$ and 10×10^{-2} this variation of K must amount to 6.5 per cent. and 13.5 per cent when the flame diameter varies from 3 cm. to 5 cm. Secondly, there is a systematic and apparent decrease of K with increase of v/δ (R remaining constant). For a variation of 5 to 12×10^{-2} , this drift will be of the order of 16 per cent. (see Fig. 12) for flames of 4 cm. diameter. (For flames of 2 cm. this drift would reach the value of 26 per cent.)

§ To be published shortly.

4. The Partial Pressure and Concentration Distribution of Sodium Vapour.

The pressure of sodium vapour at the nozzle mouth p_T is calculated from the temperature of the sodium vessel. The actual p_T differs, however, from the calculated value in so far as back diffusion of halogen into the nozzle against the carrier gas stream occurs. This back diffusion is governed by the equation:—

$$c_x = c_0 e^{-vl/D} \quad (5)$$

where c_0 is the halogen concentration directly in front of the nozzle, and c_x that in the nozzle, at a distance l from the nozzle mouth.

We should, therefore, expect that below the lower critical value of v/δ there will be an apparent increase in reaction velocities with decrease in v/δ and also with diminution of flame radius (variation of c_0). There are two ways of removing these uncertainties: the suppression, as far as possible, of "back diffusion" or the determination of the real p_T value by calculations on the lines of equation (5). We preferred the first method.

The usual value of p_{HI} outside the reaction zone is 10^{-2} . If there is a 90 per cent. impoverishment directly in front of the nozzle, the halogen concentration there will be equal to the theoretical sodium concentration (*i.e.*, 10^{-3}) and in the case of comparatively slow reactions, the total reaction in the nozzle can then only lead to a small error in p_T . A 90 per cent. halogen impoverishment according to Fig. 10 corresponds to $v/\delta = 5.5 \times 10^{-2}$, and for this reason we have selected this as the "lower critical" value of v/δ .

This lower critical v/δ value can be considered only as a standard for reactions of mean inertia (*i.e.*, with a collision number of about 5×10 to 5×10^3).^{*} For collision numbers below 5×10 the reaction in the nozzle has considerable influence on p_T , and the reaction velocities appear much too large. To a certain extent the difficulty can be overcome by the choice of a greater v/δ value for the lower limit, but in doing this, the region in which K is relatively constant is narrowed and this reduces the range of experimental conditions. In the case of high reaction velocities it is also necessary to suppress p_{HI} very strongly below 10^{-2} in order to get flames of satisfactory size, and this introduces a further difficulty, since the magnitude of p_{HI} outside the reaction zone approaches that of p_T . If, on the other hand, the collision number is much greater than 5×10^3 , then in spite of using heavier carrier gases one is obliged to give p_{HI} a value much greater than 10^{-2} to obtain a sufficiently small flame. If p_{HI} reaches or exceeds the value 10^{-1} , then the halogen concentration at the nozzle is ten times greater than that of the sodium. The small sodium reaction (for reaction of high inertia) cannot compete with the effect of the great penetration of halogen into the nozzle, since the rapidly occurring wall reaction can here assume great proportions. Here, again, one would expect a very strong decrease in K with increase in v/δ , and this is found to be the case. Thus, in very slow reactions the diffusion method cannot give accurate results.

The distribution of the sodium vapour in the reaction zone is also important, but it cannot be experimentally determined because of its small partial pressure. However, the non-symmetrical distribution of the sodium and halogen are fundamentally bound up with one another and with the permitted v/δ region from 5.5 to 12×10^{-2} , in which equation (1) is approximately satisfied. We can, therefore, neglect the non-symmetry of the sodium distribution.

^{*} This follows from results to be published later.

5. The Influence of the Halogen Compound on the Diffusion Constant.

The last question to be considered is that of the influence of the halogen compound on the diffusion coefficient (see equation (2)).

V. Hartel, Meer and Polanyi have already tried to eliminate this factor ; they studied the influence of pentane (as a chemically inert model substance for organo-halogen compounds) on the diffusion of sodium in nitrogen or hydrogen. Their main results (*loc. cit.*² Figs. 3 and 4) showed that the Tr-HI mixture would have great influence on δ for the system Na—Tr—HI. The velocity constant K was corrected by means of the calibration curves obtained with pentane. In this way certain drifts of the K values with experimental conditions became less, and in some cases disappeared. A more extensive examination of this particular question, however, showed that here one is dealing with the superposition of a real and an apparent drift in opposite directions. The drift of K with increasing flame size certainly becomes weaker if the mean p_{HI} values increase. It, however, not only disappears for certain p_{HI} values, but inverts and grows again in the opposite direction if p_{HI} increases still further. This is quite incompatible with the actual relationships in the flames. It is comprehensible on the assumption that the variability of δ is much higher than is actually the case.

This assumption is strongly supported by the experimental results given in Fig. 5. They show :—

(1) A negligible influence of the mixture ratio on the diffusion constant in the two gas systems $\text{N}_2 - \text{HI}$, and $\text{H}_2 - \text{HI}$. The values of δ were calculated without taking account of the mixture ratio. The p_{HI} value varied from 12 per cent. to 40 per cent. in the case of N_2 and from 2.4 per cent. to 16 per cent. in the case of H_2 . Nevertheless, the scattering of the points is not systematic, showing that any effect on δ due to the mixture ratio is less than the experimental accuracy under the conditions of the velocity constant experiments. Thus our results, as well as those of other authors, do not accord with the classical theoretical conclusion of O. E. Mayer :—

$$\delta : \delta' = m' : m$$

(m = molecular weight).

(2) In the presence of sodium vapour $\delta_{\text{Tr-HI}}$ remains practically unaltered (two points in Fig. 5 representing a halogen concentration of 45 per cent. and 70 per cent. and a sodium concentration of 0.1 per cent.). The triple system, therefore, behaves like a gas-pair, at least under the conditions of the velocity constant experiments.

This contradiction between our results and those of Hartel, Meer and Polanyi can be explained by the fact that the sodium partial pressure in velocity constant measurements is negligible (0.2 per cent. to 0.02 per cent. of the total pressure), whereas in their calibration experiments so small a value of p_{Na} could not be chosen ; it was over 10 per cent. of the total pressure. For the relationship in a triple system we obtain the equation (simplified) :—

$$\delta_{\text{Na-(Tr+HI)}} = \frac{1}{3N} \cdot (c_{\text{Na}} l_{\text{Na}} N_{\text{(Tr+HI)}} + \bar{c}_{\text{TrHI}} \cdot \bar{l}_{\text{TrHI}} \cdot N_{\text{Na}})$$

where l is the mean free path, c the molecular velocity, and N the

A discussion of this equation shows that the superimposed influence of two mixture ratios, though it is small for a gas pair, ought to preponderate in a triple system to give curves like those obtained by Hartel, Meer and Polanyi. But under experimental conditions where $N_{\text{Na}} < 10^{-3}N$ the above equation takes the simpler form :—

$$\delta_{\text{Na-(Tr+HI)}} = \frac{1}{3} c_{\text{Na}} l_{\text{Na}} N_{\text{(Tr+HI)}}$$

and the complex function of l_{Na} is simplified to :—

$$l_{Na} = \frac{3\sigma_{Na}^2}{\left[3c_{Na}^2 + \left(\frac{c_{HI} + c_{Tr}}{2}\right)^2\right] N_{(Tr+HI)} \Pi \left[\sigma_{Na} + \left(\frac{\sigma_{HI} + \sigma_{Tr}}{2}\right)\right]^2},$$

where σ is the molecular diameter.

The remaining influence of the mixture ratio (which is practically that of a two-gas system) must disappear completely if there is a great similarity between those properties of the halogen compound and carrier gas which are of interest in this case (c , σ). In this case, δ will be nearly invariable in the system Na—Tr—HI, whatever may be the mixture ratio Tr—HI (p_{Na} being < 1 per cent.).

Although the possible variation of δ is far less than was admitted previously, its *drift with the mixture ratio* cannot be completely neglected. This drift will always produce a weak drift of the K values which must be avoided. The more important fact is that, by calculating with one standard δ -value only, the variation of δ with the *nature of the halogen compound* would be negligible. For instance, from the following variation of δ with increasing length of carbon chain :—

$H_2 - CH_4 = 2.11$ (523°); $H_2 - C_2H_6 = 1.37$ (523°);

$H_2 - C_3H_8 = 1.23$ (550°),

it is easily realised that an observed small variation of K with rising length of the carbon chain of organo-halogen compounds could actually be due to the error introduced by the neglect of the δ variation.

Since the calculation of these δ variations on the basis of revised calibration curves is for many reasons excluded, they must be avoided experimentally. To do so we tried to obtain the above-mentioned ideal condition of great similarity between the carrier gas and the halogen compound for c and σ . As it is impossible to use a different carrier gas for every halogen compound, one was chosen such that δ_{Na-Tr} lies *within* the limited range caused by the variation of δ_{Na-HI} with the nature of the halogen compound. This condition is fulfilled by pentane. We have the following approximate values for :—

Na — $H_2 = 3.14$; Na — $CH_4 = 1.27$; Na — $N_2 = 0.84$;

Na — $C_5H_{12} = 0.53$.

On the other hand, for the lightest halogenated organic compound, CH_3Cl , we obtain the approximate value: $\delta_{Na-CH_3Cl} = 0.65$. Since the lengthening of the carbon chain and also the introduction of more or heavier halogen atoms reduces the value of δ_{Na-HI} , pentane is actually situated within the possible range.

A closer examination of the facts shows that the *change of K* , (obtained using a constant $\delta_{Na-C_5H_{12}-HI}$ value), *with the nature of HI*, seldom exceeds the accuracy of the diffusion method. As regards the *influence of the mixture ratio*, we found that δ remains constant within a range of p_{HI} variation from 0 per cent. to 50 per cent. if δ_{Na-HI} is smaller than 0.56; if it exceeds this value, the drift of δ is negligible for the variation of p_{HI} from 5 per cent. to 10 per cent. Using the most unfavourable HI-compound, CH_3Cl , the drift of δ within this range amounts to 6 per cent.

For rapid reactions the pentane pressure must be reduced below 1 mm. to obtain large enough flames. Under these conditions many technical difficulties arise connected with the regulation and maintaining constant of small pressures. Nitrogen and hydrogen therefore were still used as carrier gases, thus also allowing a larger experimental range. To exclude any influence of the halogen on δ in this case, it was necessary to keep p_{HI} sufficiently small compared with p_{Tr} . In the presence of N_2 , p_{HI} must remain below 3 per cent., and in the presence of H_2 below 0.1 per cent. of the total pressure. Within these limits the variation of p_{HI} remains

negligibly small. For the most part (principally for N_2) this limitation of p_{HI} is already determined by that necessary to eliminate the influence of back diffusion.

6. Conclusion.

The most important result is that the Hartel-Polanyi diffusion method can be used in its now altered form for quantitative determinations of reaction velocities. This holds for reactions of collision number between 5×10 and 5×10^3 , if the following experimental conditions are fulfilled:

(a) The distribution of the reaction gases in the flame must correspond sufficiently to the assumptions made in equation (2), *i.e.*, for v/δ values below 12×10^{-2} .

(b) The halogen partial pressure must be kept so small as to eliminate error through the back diffusion of HI into the nozzle as much as possible. This condition is fulfilled for v/δ values greater than 5×10^{-2} if the halogen partial pressure does not exceed a small percentage of the total pressure in the case of H_2 or N_2 and 10 to 20 per cent. in the case of pentane as carrier gas.

(c) Flames must be greater than 3 cm. or better greater than 3.5 cm. diameter. In this case the approximation of the actual conditions to those of uniform halogen distribution in the flame and of the smallest possible back diffusion is the best. Smaller flames, on the other hand, fail in both respects, even if the v/δ value lies within the permitted range.

(d) The influence of the halogen compound on the diffusion constant of sodium vapour in the carrier gas has to be completely eliminated. This is possible by the use of pentane as a carrier gas, or in the case of N_2 or H_2 by a stricter limitation of the variation of p_{HI} .

(e) The accurate determination of p_{HI} by taking into consideration the effect of slip in the capillaries, and also the reproducibility of the sodium pressure in the sodium oven.

The discussion of the various sources of errors has shown that the reaction velocities obtained by this method ought to differ by little more than 100 per cent. from the absolute values, if the best experimental conditions are used. In this case also, the middle term of equation (1) is negligible, and therefore, experiment is in very good agreement with the theoretical principles of the method.

The above experiments were carried out in the Kaiser Wilhelm. Institut für Physikalische Chemie at Berlin-Dahlem from 1931 to 1933. I should like to express my gratitude to Professor Polanyi for his constant advice in theoretical and experimental matters. I also wish to thank the Liebig Gesellschaft zur Förderung der deutschen Wissenschaft, and the Central British Fund for German Jewry for grants, and Dr. A. G. Evans who translated this paper from the German.

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THE REACTION OF SODIUM ATOMS WITH THE OXIDES OF NITROGEN, NITROMETHANE, ETHYL NITRATE AND AMYL NITRITE.

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The development by Beutler and Polanyi,¹ and Hartel and Polanyi² of a technique for the study of atomic reaction has enabled a systematic study to be made of the reaction of sodium atoms with the halogens, hydrogen halides, a large number of inorganic halides, and a wide variety of organic halogen compounds.³ Parallel to these experiments, theoretical developments, following from the pioneer work of Heitler and London, have proceeded so rapidly that the fundamental chemical principles of these atomic reactions are clearly understood.⁴

In the present work similar experimental methods have been used to study the reactions of sodium atoms with the oxides of nitrogen and compounds containing the —N=O linkage. Such reactions present a new feature in so far as the attack of the sodium is at a multivalent atom.

Experimental.

The experimental method used was that of the diffusion flame of Hartel and Polanyi,² incorporating the improvements in apparatus and experimental conditions as recommended by Heller.⁵ The method of carrying out the experiments was precisely as described by these authors and no further details will be given in this paper.

Preparation of Materials.

Nitrous Oxide was obtained from a cylinder and was more than 99 per cent. N_2O . It was condensed out in liquid air, nitrogen being removed by evacuation, and was finally distilled from -80° to -40° C.

Nitrogen Peroxide was made by heating lead nitrate. This gas was dried by passage over phosphorus pentoxide and was condensed by liquid air. After evacuation to remove oxygen and nitrogen, the nitrogen peroxide was redistilled into the apparatus.

Nitromethane, Ethyl Nitrate and Amyl Nitrate.—High-grade commercial products were dried and distilled before use.

Nitrogen was obtained from a cylinder and was purified by passage over molten sodium at 300° C.

Nitric Oxide was made as described in the following paper (p. 1580).

¹ Beutler and Polanyi, *Naturwiss.*, 1925, **13**, 711.

² Hartel and Polanyi, *Z. physikal. Chem.*, B, 1930, **11**, 97.

³ Polanyi, "Atomic Reactions" (Williams and Norgate), 1932; Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.

⁴ Eyring and Polanyi, *Z. physikal. Chem.*, B, 1931, **12**, 279; Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 1375.

⁵ Heller, *Trans. Faraday Soc.*, in press.

Results.

Reaction Velocities.

The reaction velocities of atomic sodium with nitrous oxide, nitrogen peroxide, nitromethane, ethyl nitrate and amyl nitrite have been measured at temperatures *circa* 260° C. The results are set out in Table I. The velocity constants were calculated in the usual way from the formula

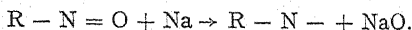
$$k = \frac{(\ln p_{\text{Na}}/p_0 - \ln R/r)^2}{(R - r)^2} \cdot \frac{\delta}{p_x} \cdot \frac{1}{T} \quad (1)$$

where p_{Na} and p_0 are the pressures of sodium at the centre and at the edge of the flame respectively; R the radius of the flame and r that of the nozzle; δ the diffusion constant of sodium in nitrogen; p_x the pressure of the reaction partner in the reaction vessel, and T the absolute temperature.

TABLE I.—REACTION OF SODIUM WITH NITROGEN-OXYGEN COMPOUNDS
(using nitrogen as carrier gas).

Reaction Partner.	Pressure of Sodium Vapour at Nozzle Mouth, mm. 10 ³ .	Temperature of Reaction Zone, °C.	Streaming Velocity of Carrier Gas, mol./sec. 10 ³ .	Rate of Flow of Reaction Partner, mol./sec. 10 ³ .	Total Pressure in Reaction Vessel, mm.	Partial Pressure of Reaction Partner, mm.	Diffusion Coefficient of Sodium, mol./cm. ² /sec.	Radius of Flame, cm.	Velocity Constant, c.c. mole ⁻¹ sec. ⁻¹ 10 ⁻¹² .	Collision No.	Activation Energy, cal.	Mean Activation Energy, cal.
N ₂ O	10.6	262	1600	5.2	3.82	0.0123	134	1.34	9.8	40	3,900	3,800
	7.5	253	1100	3.2	3.65	0.0102	137	1.4	9.8	40	3,900	
	107.9	275	1500	4.4	3.83	0.0109	128	1.43	16.8	24	3,500	
	3.2	262	1600	4.4	3.95	0.0110	129	1.25	8.4	50	4,200	
	3.6	260	1300	4.0	3.69	0.0110	138	1.11	11.6	36	3,800	
	3.7	260	1400	4.0	3.65	0.0109	139	1.03	14.1	29	3,600	
NO ₂	2.5	252	1100	1.0	3.12	0.0030	160	0.95	58.1	7	2,000	2,400
	2.2	253	1100	1.0	3.19	0.0030	156	1.12	40.2	10	2,400	
	2.1	249	1100	1.0	3.26	0.0030	151	1.02	45.6	9	2,300	
	2.4	253	1600	1.7	3.87	0.0041	129	0.97	32.6	12	2,600	
	2.2	254	1600	1.7	3.87	0.0041	129	1.38	15.4	16	2,900	
CH ₃ . NO ₂	2.0	255	1300	0.8	3.45	0.0021	145	1.12	51.7	8	2,200	2,300
	2.0	255	1200	0.8	3.49	0.0021	143	1.29	38.2	11	2,500	
	2.0	255	1100	0.7	3.26	0.0021	154	1.29	41.0	10	2,400	
	2.3	255	1200	0.6	3.26	0.0017	154	1.31	52.8	8	2,100	
C ₂ H ₅ . NO ₂	2.0	254	1100	0.5	3.28	0.0015	152	1.53	39.8	10	2,400	2,350
	1.9	253	1300	0.5	3.49	0.0013	143	1.52	43.8	9	2,300	
C ₅ H ₁₁ . ONO	1.6	249	1900	1.2	4.16	0.0027	118	0.94	42.1	10	2,400	2,800
	2.0	253	1800	1.2	4.06	0.0027	123	1.4	21.5	18	3,100	

It will be shown that the measured velocity constants refer to the primary reaction.



The collision number (Column 11, Table I) was calculated using a collision diameter of 5×10^{-8} cm. and the activation energies were determined from the relationship

$$\frac{\text{Effective number of collisions}}{\text{Total number of collisions}} = e^{-E/RT}.$$

The reactions are all slightly too fast to come within the range (50-5000 collisions) in which the method may be used quantitatively. We estimate the accuracy to be about 50 per cent.

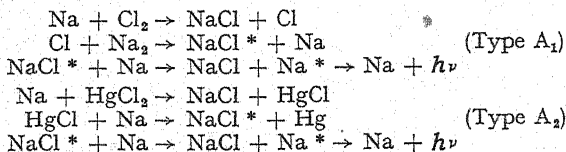
Chemiluminescences.

The reactions of both nitrous oxide and nitrogen peroxide were accompanied by a marked chemiluminescence, that with the former gas being much more intense. The intensity of the luminescence was considerably increased when the nitrogen pressure was reduced to below 1 mm. pressure. Further the luminescent flame was of the same shape as the reaction zone ("flame") as observed in the usual way with the resonance lamp but was much smaller (see Fig. 1). In the case of nitrous oxide the radius of the luminescent flame was estimated to be about quarter that of the normal flame. No similar estimate could be made for nitrogen peroxide on account of the small intensity of the luminescence. It was also found that over-heating the reaction zone produced a marked decrease in the intensity (observed visually) of the luminescence. For example, with the nitrous oxide reaction, by raising the temperature of the reaction zone from 250° C. to 450° C., keeping the temperature of the sodium container at 250° C., the luminescence gradually diminished and at 450° C. was scarcely visible. A decrease of the intensity of the chemiluminescence was also observed when a small amount of nitric oxide was admixed with the nitrous oxide. In these experiments the nitrous oxide was not introduced in the usual way,^{3, 5} but the gas containing either 10 or 20 per cent. nitric oxide was allowed to flow into the reaction vessel from a gas burette.

In order to render the luminescence more intense some observations were made by means of the method of "highly attenuated flames."⁶ The reacting gas was admitted directly into the sodium vapour from a nozzle without the use of nitrogen. A spectroscopic examination of the luminescent radiation showed this to be the D line of sodium.

Reaction Mechanism.

The above observations on the luminescence of the reactions reveals the nature of the chemical changes taking place. Such chemiluminescences accompanying the reactions of sodium atoms are well known and seem to be of three different types. The first type initially observed by Haber and Zisch⁷ and elucidated by Beutler and Polanyi⁶ occurs in the reaction with the halogens and certain inorganic halides. The mechanism of this luminescence, which gives rise to the sodium D line, is as follows:—



⁶ Beutler and Polanyi, *Z. physikal. Chem.*, B, 1928, 1, 3.

⁷ Haber and Zisch, *ibid.*, 1922, 9, 302; Beutler and Polanyi.⁶

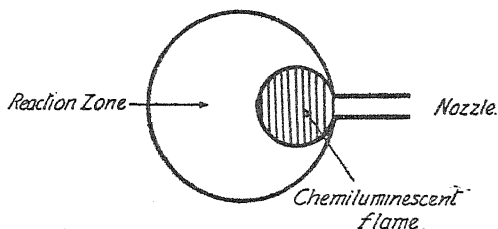
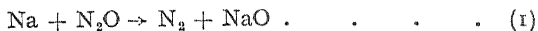


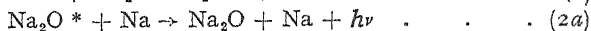
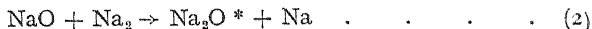
FIG. 1.—Reaction zone (or "flame") observed by means of a sodium resonance lamp. Chemiluminescent flame (shaded area) observed without lamp.

the process of the excitation consisting in a collision of the activated NaCl^* with a normal sodium atom. The other two types of luminescence (type B and C) which have been observed with other inorganic halogen compounds exhibit a continuous⁸ (B) and a banded⁹ (C) spectrum respectively. It is evident therefore that the luminescences of the reactions of the nitrogen oxides belong to type A.

We propose to show that the observed chemiluminescence can be explained if the reaction occurs in stages analogous to type A, namely the primary reaction



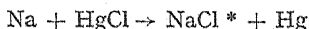
is followed by the secondary reactions



which produce the luminescence. That the luminescence arises from a reaction involving Na_2 molecules is strongly supported by the two observations referred to previously, *viz.* :—

(1) the decrease of luminescence which occurred on raising the temperature of the reaction zone. It has been shown in earlier work that this phenomenon is characteristic of the reactions of sodium molecules and as in those cases the observation may be explained by assuming that the increase in temperature dissociates the Na_2 molecules and thus decreases the light emitting reaction.

(2) The much decreased diameter of the chemiluminescent flame compared to that of the normal "flame." This may be accounted for by the fact that the concentration of sodium molecules is only appreciable in the region of the nozzle, and that outside of this region the concentration is insufficient to give rise to visible luminescence. This is so because the sodium molecules which are present in a very small concentration compared to that of the sodium atoms are rapidly removed by reaction on leaving the nozzle and are not reformed in the flame. This explanation is substantiated by the following observations. In the case of the diffusion flames in chlorine gas we observed that the chemiluminescence flame, which is known to be produced by secondary reaction with sodium molecules, was visible only in the region of the nozzle, and was much smaller than the resonance flame. With mercuric chloride and sodium in which case the light producing reaction is

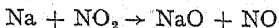


and does not involve sodium molecules, we observed that the chemiluminescent "flame" and the "flame" observed with the resonance lamp were about the same size.

It can be shown furthermore, that supposing (1) is the primary reaction then sufficient energy will be released in reaction (2) to excite the sodium atoms. This may be deduced in the following way: since the reaction of sodium atoms with NO_2 has a very small activation energy and this reaction must be either exothermic or at least have a zero heat of reaction. Now since the thermochemical process¹⁰



is well established and the reaction



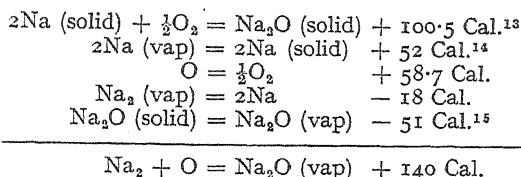
is, on the evidence of reaction velocity measurements reported in the paper, at least thermo-neutral, we can say that the lower limit of the heat of dissociation of NaO (D_{NaO}) is 72 Cal. This is a likely value as shown by the following evidence:

⁸ Polanyi and Schay, *ibid.*, 1928, 47, 814.

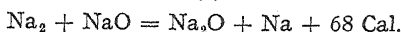
⁹ Frommer and Polanyi, *Z. physikal. Chem.*, B, 1930, 6, 371; Heller and Polanyi.⁵

¹⁰ Sponer, *Molekülspektrum* (Springer), 1936, p. 261.

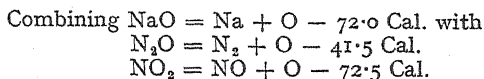
- (a) From an approximate rule of Pauling¹¹ D_{NaO} can be taken as the mean of D_{Na_2} and D_{O_2} . This gives a value of 68 Cal.
 (b) By comparison with analogous molecules¹² another approximation to D_{NaO} may be taken as half the heat of formation of Na_2O from Na_2 and O and this again is about 72 Cal.
 The heat of reaction (2) can now be estimated from D_{NaO} and the heat of formation of sodium monoxide, *viz.* :—



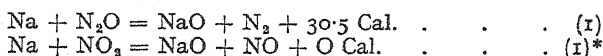
which gives for the heat of reaction (2)



This is more exothermic than 48.5 Cal.—the energy of excitation of sodium atoms.

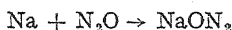


it is seen that reactions (1) or (1) *

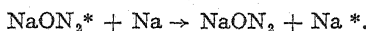


are not sufficiently exothermic to allow of the direct production of the luminescence in the primary reaction.

It should be pointed out that the only possible alternative to (1) would be

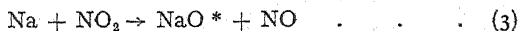


and in this case the luminescence would have to be ascribed to

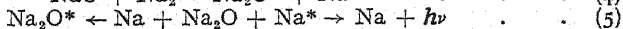
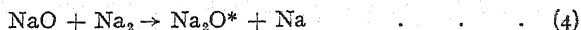


This mechanism can be ruled out since it fails to account for the experimental facts—the decrease in luminescence with temperature and the decreased size of the chemiluminescence flame compared to that of the normal flame (see p. 1574). Furthermore, if such a reaction occurred it is unlikely that the energy produced would be as great as 48.5 Cal.

Exactly analogous arguments (which we shall not give here) may be brought forward to explain the chemiluminescence of the reaction of nitrogen peroxide. The measured rate is assumed to refer to the primary reaction



followed by the light producing reactions



Reaction (3) is faster than the corresponding reaction for nitrous oxide, whilst reactions (4) and (5) are identical with (2) and (2a). It was to be expected, therefore, that the luminescence of the nitrogen peroxide

¹¹ Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 3570.

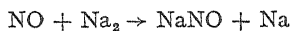
¹² *E.g.* $\text{OH} = \text{O} + \text{H} - 103 \text{ Cal.}$ $\text{H}_2\text{O} = 2\text{H} + \text{O} - 217 \text{ Cal.}$

¹³ Landolt-Bornstein Tabellen, II, 1504.

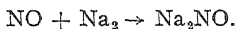
¹⁴ Ladenberg and Theile, *Z. physikal. Chem.*, **B**, **7**, 174, 1930.

¹⁵ The heat of vaporisation of Na_2O at 1200° C. is 38.5 Cal. (Preston, *Trans. Faraday Soc.*, 1935, **31**, 776). The value at room temperature, we estimate, is 15 Cal. greater than this.

reaction would be at least of the same order as that of the nitrous oxide reaction. It is found, however, that the luminescence of the nitrogen peroxide reaction is very much less than that of nitrous oxide for similar amounts of reaction. This we believe is due to the participation of the nitric oxide formed in the primary reaction (3), in a secondary reaction leading to the destruction of sodium molecules. We assume these reactions are

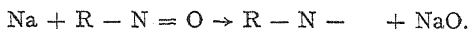


and possibly

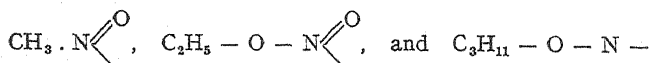


Evidence for the specific depressing influence of nitric oxide on the luminescence has been supplied by the fact mentioned previously that the luminescence of the nitrous oxide reaction is reduced by the addition of nitric oxide to the nitrous oxide. Under the conditions in which these experiments were carried out the reaction of nitric oxide with sodium was almost negligible and the slight quenching of the sodium fluorescence by the nitric oxide was not sufficient to account for this observation.¹⁶

It is assumed that the mechanisms of the reaction of nitromethane, ethyl nitrate and amyl nitrite are similar to those of nitrous oxide and nitrogen peroxide and may be represented by the general equation



The absence of chemiluminescence (as examined only in the diffusion flame) presents a difficulty, but we suggest that it can be explained by the reaction of the radicals

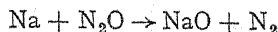


with sodium molecules (Na_2) which would inhibit the secondary reactions. It may be that the luminescence is still present but that is too weak to be observed by this method.

Theoretical.

Activation Energies.—It is important to the general theory of chemical reaction to explain the high collision yield and low activation energies of the various reactions studied, all of which involve an attack at the $-\text{N} = \text{O}$ bond.

We shall consider the reaction



in some detail and compare the other reactions with this.

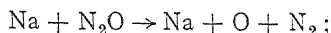
From our previous knowledge of this type¹⁷ of reaction we can infer that the true energy surface of this change would be obtainable from two intersecting energy surfaces, one for the interaction of the sodium atom with the nitrous oxide molecule and the second for the reaction between the products NaO and N_2 . The two surfaces will be fixed relative to one another by the heat of reaction and the activation energy can be obtained in the usual way from the lowest point of intersection of the two surfaces. In this paper we do not propose to calculate the complete energy surface but simply to obtain a numerical estimate of the activation energy by evaluating the activation energy

¹⁶ It was found that NO gave no "flame" at low inert gas pressures as used in these experiments. At the same time a quenching was noticeable but this produced only a slight decrease in the intensity of the light.

¹⁷ Ogg and Polanyi⁴; Evans and Evans, *Trans. Faraday Soc.*, 1935, **31**, 1400.

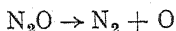
for a reaction path which we choose in a particular way. This reaction path is characterised for the purpose of calculation by the particular transition state corresponding to this path. The state which we select as our transition state is one in which the Na — O separation is that of the normal NaO molecule. The true reaction path which gives the true activation energy of the reaction cannot have a higher activation energy than the above, and thus our calculation will give upper limit of the activation energy.

We can take as our section of the first surface that of the reaction



this may be represented diagrammatically by curve *a* of Fig. 2. This curve was obtained by taking a section through the transition state of the chosen reaction path corresponding to the configuration in which the sodium atom attacking along the axis of the N_2O molecule is brought up to a distance in which the separation Na . . . O is equal to $r_0(\text{NaO})$, all other distances being kept at their normal separations in the N_2O molecule.

Curve *b* represents the initial state of the system in which the sodium atom is at infinity. This curve will therefore be the potential energy curve for the dissociation of nitrous oxide according to



and has been calculated by Stearn and Eyring.¹⁸ The energy difference *l* between the minima of curves *a* and *b* will be the work necessary to bring the sodium atom up to the critical separation $r_0(\text{NaO})$. Furthermore, if *l* is small curve *a* in the region of the minimum will have the same shape as that of curve *b* and may be plotted therefore by raising curve *b* bodily a distance equal to the energy *l*. We may conclude that since it is most unlikely that the Na — O separation in the transition state would be as small as $r_0(\text{NaO})$ (the value we have used), that the estimated activation energy will be an upper limit.

¹⁸ Stearn and Eyring, *J. Chemical Physics*, 1935, 3, 778.

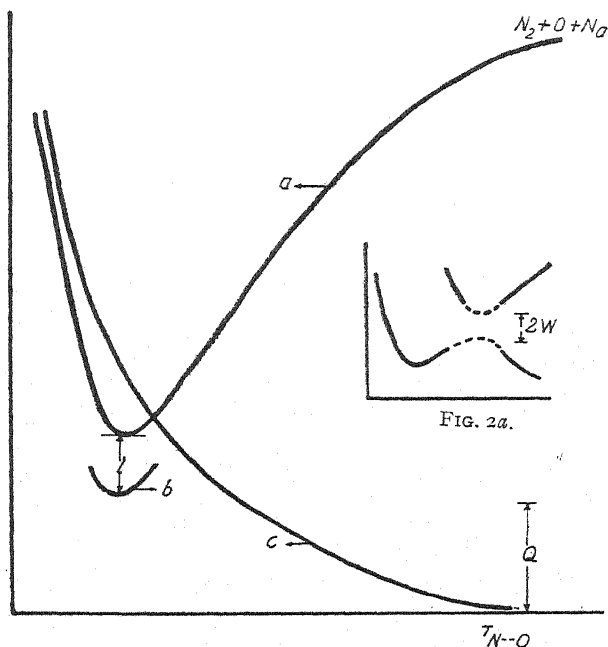


FIG. 2.

The value of l is determined by the (repulsive) energy to bring the sodium atom up to a separation $r_{0(\text{NaO})}$ and this we have taken as 28 per cent. of the interchange binding¹⁹ of NaO. This equals 12 Cal. If polarisation forces are taken into account this value will be reduced and may even become negative.

The section of the second surface will correspond to the repulsive state between NaO and N₂ and will be fixed in relation to b by an energy difference equal to the heat of reaction (28 Cal.). This curve will have two distinguishing features in that it becomes asymptotic at about the same —N—O— separation as curve b does, *viz.*, 3.1 Å. and that at small separation $r_{\text{N-O}}$ the repulsive curve approximates closely to curve a . It follows that the repulsive curve will have the shape c and in estimating this curve we have taken 28 per cent. of the Morse curve value for nitric oxide.

As mentioned previously, the assumption employed in calculating l causes our estimate to be an upper limit. Detailed calculations carried out for the reaction $\text{Na} + \text{RCl}$ show that the normal nuclear separation ($\text{Na} - \text{Cl}$) in this case is reached without any expenditure of energy. Similar calculations in the present case would lead to a reduction in the height of crossing of the curves a and c .

The activation energy is necessarily lower than the crossing point of curves a and c since their intersection results in the well-known splitting as represented by the dotted lines Fig. 2*a*, the curves being separated from each other by the perturbation energy W . The reactions correspond to the passage of the system from surface b along the dotted curve * to surface a .

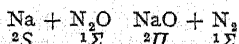
The significant feature of our diagram, in spite of the approximate nature of the numerical data, is that the transition state proves to be in the neighbourhood of the minimum of curve b and therefore the reaction will have a small activation energy. The reaction of nitrogen peroxide is analogous to that of nitrous oxide and our mechanism will again give a small activation energy although the finer differences between these two reactions must await future developments of the method.

Activation Energy and Heat of Reaction.

In contrast to the reactions of the alkyl halides with sodium it was surprising to find that the variation of structure from the nitrogen oxides to the organic nitrates and nitric compounds caused no appreciable change in the activation energy. Although no exact thermochemical data is available, general chemical evidence seems to indicate that the —N=O bond energy varies appreciably as one passes from the nitrate to the nitro-compound. The non-observance of any parallelism between the bond strength of the —N=O and the activation energy can be

¹⁹ This follows from the formula of perfect pairing $W = Q + \Sigma J_{ii} - \frac{1}{2} \Sigma J_{ij}$. For a repulsive state and assuming 15 per cent. coulombic energy, the repulsive energy at any separation is 28 per cent. of the interchange binding for that separation (see also ref. 18).

* In order to account for the high collision yield of the reaction it is necessary to postulate that no restriction is placed upon the passage of the system from one energy surface to the other. Since there is no change of multiplicity,



there will be no restriction due to an electronic transition.

readily correlated with the mechanism of the reaction as depicted in Fig. 3. Thermochemical evidence indicates that the —N=O bond strength is less than 70 Cal. and therefore all the reactions are exothermic.

Furthermore, the repulsive energy surface c will be to a first approximation the same in all the cases and therefore the variation for the —N=O bond strengths would result solely in an upward or downward displacement of the potential curve a . For example, we represent the three types of binding in the nitrate, nitrocompound, and nitrite by the curves a_1, a_2, a_3 . Now if $l_1 = l_2 = l_3$ it follows directly from the diagram that although the heat of reaction

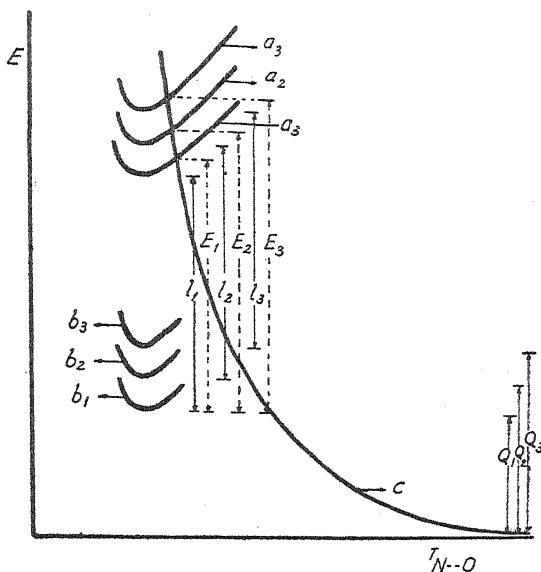
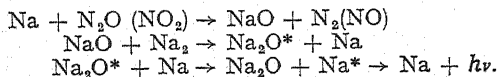


FIG. 3.

Q_1, Q_2 , and Q_3 differ considerably, the activation energies E_1, E_2 and E_3 are all equal. It is important to realise that this is so only because the crossing of the curves occurs in the region of the minimum. The fact that our determined activation energies are small shows that this must be the case. If the crossing point occurred on the steeper portion of curve a then as shown by Ogg and Polanyi²⁰ and by Horiuti and Polanyi²¹ a change of activation energy with heat of reaction would be observed.

Summary.

The rates of reaction of sodium vapour with nitrous oxide, nitrogen peroxide, nitromethane, ethyl nitrate and amyl nitrite have been studied. An important characteristic of the two former reactions is a marked chemiluminescence which has been shown to be produced by secondary reactions with sodium molecules. The following mechanism is postulated



The theory of the reaction is also discussed.

*The University,
Manchester.*

²⁰ Ogg and Polanyi.⁴

²¹ Horiuti and Polanyi, *Acta Physicochimica, U.R.S.S.*, 1935, 2, 505.

THE KINETICS OF BIMOLECULAR ASSOCIATION REACTIONS.

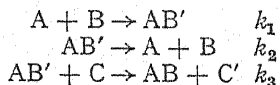
THE RATES OF REACTION OF SODIUM ATOMS WITH OXYGEN, NITRIC OXIDE AND OTHER OXIDES.

By C. E. H. BAWN AND A. G. EVANS.

Received 12th November, 1937.

It is a well-established fact that the bimolecular association of two atoms to form a homopolar molecule is a very improbable process, and that such reactions invariably occur through a triple body mechanism.¹ If the pressure of the third body is high enough it should be possible to attain the condition where every diatomic complex will, during its lifetime, be stabilised. Under these conditions the rate of reaction will be independent of the third body and will follow a bimolecular law. The condition, however, has never been realised experimentally since with complexes of such small lifetimes the pressure region in which it would be expected is much higher than that normally employed in kinetic experiments with atoms.

When, on the other hand, we extend these considerations to the association of molecules, we must introduce the additional condition that it is no longer necessary to remove the energy of association from the complex since now we have the possibility that this excess energy may be taken up by the internal degrees of freedom of vibration of the molecule. On account of this redistribution of energy among the degrees of freedom, the average lifetime of the molecule is considerably increased and this time may be great enough to ensure the subsequent stabilisation of the molecule by collision. The bimolecular velocity constant will, however, fall off as the pressure is decreased and the reaction will ultimately become termolecular. The general equation for the rate of this type of reaction may be derived as follows: consider the reactions



where A, B are the reactants and C represents the molecule acting as the "third body." Setting up the stationary concentration of (AB') we have

$$k_1(A)(B) - k_2(AB') - k_3(AB')(C) = 0$$

now the measured rate of reaction

$$\begin{aligned} \frac{d(AB)}{dt} &= k_3(AB')(C) \\ &= k_1(A)(B) - k_2(AB'), \end{aligned}$$

¹ Kassel, *Kinetics of Homogeneous Gas Reaction* (Chem. Catalog. Co.), page 44.

and when the pressure of C is high, k_2 is small and therefore

$$\frac{d(AB)}{dt} = k_1(A)(B),$$

that is, the reaction becomes bimolecular.

In the present work in which the rates of reaction of sodium with a number of oxides and sulphides have been investigated, these conditions have been realised and in the reaction of nitric oxide and oxygen we have determined both k_1 , and the ratio k_2/k_3 . From the latter ratio by making certain assumptions about k_3 we have determined the average lifetime of the associated complex.

Experimental.

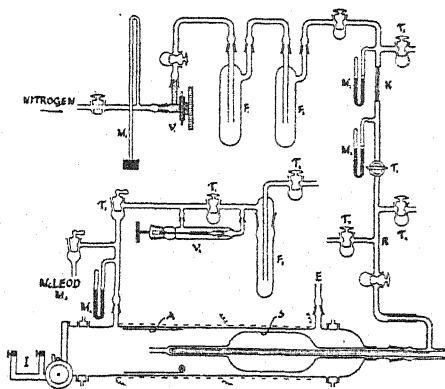
Preparation of Materials.

Nitric Oxide was prepared by the method of Johnston and Giaque² by the action of a 50 per cent. solution of sulphuric acid on a concentrated solution of potassium nitrite and potassium iodide. The gas was purified by passing through solutions of sulphuric acid, potassium hydroxide, and

FIG. 1. Reaction Tube and Streaming System.—

Nitrogen from a cylinder enters the system through valve V_1 and is pumped out through valve V_2 . These valves regulate the flow and the pressure of nitrogen in the system. F_1 and F_2 are traps containing sodium heated to 300° C. for removing oxygen and other reacting gases from the nitrogen. The nitrogen is saturated with sodium in the sodium container S. The temperature of the sodium, and also of the reaction zone (at the nozzle mouth) is measured by a thermocouple.

The reaction products depositing on the walls in the region of the reaction zone would cause an alteration in the intensity of the sodium resonance illuminating the reaction zone. To prevent this, the reaction products are collected on an inner cylinder A to which a piece of iron is attached. This cylinder can thus be moved by means of a magnet so as to expose a clear tube before a measurement is taken. The rate of streaming of the nitrogen is determined from the pressure difference across the calibrated capillary K. The total pressure in the reaction vessel is measured by the McLeod M_2 and, for high pressures, by the manometer M_1 . The reaction partner enters the reaction vessel through E (see Fig. 2), any unchanged reactant being condensed out in the liquid air cooled trap F_3 . The flame diameter is measured by the appliance I, the cross wires of which can be adjusted successively to the upper and lower edges of the flame. The diameter is read directly from a Vernier attachment.



finally through a trap cooled at -80° , to remove higher oxides of nitrogen. The nitric oxide was condensed in a trap cooled in liquid air, and was distilled over phosphorus pentoxide into the storage vessel.

Oxygen, prepared by heating potassium permanganate, was purified by passing it over potassium hydroxide and dried over phosphorus pentoxide.

² Johnston and Giaque, *J. Amer. Chem. Soc.*, 1929, 51, 3194.

Hydrogen Sulphide was prepared by adding calcium sulphide to a saturated solution of magnesium chloride and warming to mixture to 60°. It was dried over phosphorus pentoxide.

Sulphur Trioxide.—Solid SO_3 was purified by distillation in vacuo.

Sulphur Dioxide, obtained from a syphon, was carefully purified by fractionation.

Apparatus and Procedure.

The general lay-out of the apparatus and the experimental procedure used was essentially that of the diffusion method, as previously described.³ Since it was desired to measure reaction velocities over a wide range of pressures of carrier gas, the following modifications of the original apparatus were made. The use of a pump for circulation of the carrier gas was unsatisfactory for pressures greater than 10 mm., and a direct gas flow method was therefore substituted for the circulating method. The carrier gas (nitrogen) was taken directly from a cylinder and was pumped over the sodium by means of a "hyvac" pump, and was finally set free into the atmosphere. The gas was carefully purified in the flow line before entering the sodium vessel, and the flow over the sodium was regulated by a system of valves. The complete apparatus is shown in Figs. 1 and 2.

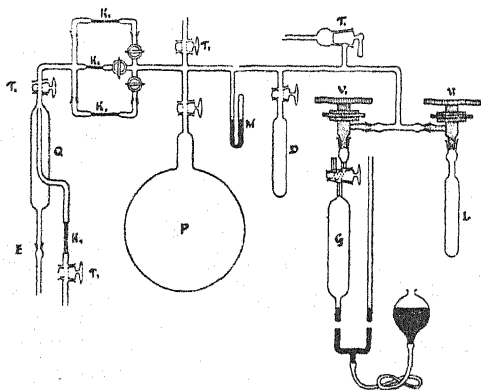


FIG. 2. Reaction Partner

System.—The reaction partner is stored in the reservoir L if it is condensable, and streams into the system through valve V_1 . If it is not condensable or is very volatile it is stored at atmospheric pressure in G, and streams into the system through valve V_2 . The reaction partner flows through the calibrated capillary K_1 , K_2 or K_3 , and enters the reaction vessel through E. The volume P (3 litres) is included in the system to reduce

irregularities of pressure. To enable the reaction partner to attain rapidly its equilibrium pressure in the reaction vessel, a tributary nitrogen stream (1/10th that of the main flow) is introduced behind the reaction partner capillaries at Q. This tributary flow increases the ease of diffusion of the reaction partner into the reaction vessel.

The sodium resonance lamp used in previous work with this method was replaced by an electrodeless discharge lamp of the type described by Fairbrother and Tuck.⁴ It was thus possible by accurate control of the temperature of the sodium and of the tuning of the oscillator circuit, to maintain the intensity of the light constant over long periods of time.

Accuracy.

Technically, with the modified streaming system there is no limit to the pressure of nitrogen that may be used, but in practice the pressure range is fixed by the speed of the reaction being measured. The principle of the flame method is to select the conditions of pressure and of streaming

³ Hartel and Polanyi, *Z. physik. Chem., B*, 1930, **11**, 97; Heller, *Trans. Faraday Soc.*, in press.

⁴ Fairbrother and Tuck, *ibid.*, 1935, **31**, 520.

such that a simple mathematical treatment of the problem is possible. In this way the simple formula (page 1572) is obtained for the velocity constant, the applicability of which is determined by the extent to which the experimental conditions approximate to the assumptions made in deriving the formula. These conditions are (1) the distribution of the halogen partner throughout the reaction zone is uninfluenced by the flow of the carrier gas from the sodium container, (2) the flow of the carrier gas is such that the sodium enters the reaction vessel solely by diffusion, and (3) that there is no back diffusion into the nozzle from which the sodium enters. The optimum conditions of streaming under which these conditions are fulfilled have been precisely fixed by Heller⁵ and his co-workers. They concluded that the velocity constants could be determined to an accuracy of 15 per cent. by working in certain regions of v/δ , where v is the linear velocity of streaming of the carrier gas and δ is the diffusion constant of the sodium, and with flames of 1.75 cm. radius or greater. These conditions have been strictly adhered to in the present experiments.

Previous studies with sodium atoms have been confined almost entirely to the bimolecular reactions of the halogen compounds. In these experiments no dependence of the rate of reaction on the carrier gas pressure was observed. However, since these measurements were made only at low carrier gas pressures it was necessary to establish this over a wider pressure range and to make sure that the pressure dependence observed in our experiments, with different substances, was not a defect of the method. For this purpose blank experiments were carried out with isobutyl chloride, this compound being selected since it reacts at about the same speed as the substances under investigation. The results are given in Table I, and the constancy of the reaction velocity constant is evident. It was found desirable in these experiments to observe the flame at constant size, and this was followed in all later work.

Results.

The results of the reactions of sodium atoms with a number of compounds are given in Table I. The data in the bottom columns (NO , H_2S , SO_2 , and SO_3) were obtained by the usual diffusion flame method using a circulating system, and those in the middle columns (Nitric oxide and oxygen) by the modified streaming method, as described in this paper. The former method was used more for a survey of the reactions of a number of compounds rather than for absolute measurements of the reaction velocity constants. The results obtained for oxygen and nitric oxide by the two methods are included in Table I. It is seen that the values determined by the circulation method are two to three times greater than those obtained by the second method. This is due to the fact that in the earlier work no attempt was made to adhere strictly to the ideal conditions necessary for accurate measurements, and that the circulation method was unsuitable for carrier pressures above 10 cm. when the best flames were obtained. The data obtained by the streaming method were determined under ideal conditions, and we estimate that the accuracy is better than 20 per cent.

All reaction velocity constants were calculated from the formula given in the previous paper (page 1571).

Oxygen and Nitric Oxide.—Neither of these gases gave a flame at low pressures of nitrogen. A measurable flame was obtained for oxygen and nitric oxide at pressures above 5 and 6 mm. respectively. Below these pressures the flame completely filled the reaction tube. An indication of reaction, at low pressures, however, was shown by the following observation: with the carrier gas flowing and the sodium filling the tube the admission of a small amount of either of these gases into the reaction

⁵ Heller, *loc. cit.*³.

TABLE I.

Reaction Partner.	Pressure of Sodium Vapour at Nozzle Mouth, mm. 10^3 .	Temperature of Reaction Zone, $^{\circ}\text{C}$.	Rate of Flow of Carrier Gas, (N_2) Mol./sec. 10^3 .	Rate of Flow of Reaction Partner, Mol./sec. 10^3 .	Total Pressure in Reaction Vessel, mm.	Partial Pressure of Reaction Partner, mm.	Diffusion Coefficient of Sodium, cm^2/sec .	Radius of Flame, cm.	Velocity Constant K , c.c. mol. $^{-1}$ sec. $^{-1}$.
Iso-Butyl Chloride.	1.64	260	3,223	37.39	10	0.115	50.81	1.75	$5.77 \cdot 10^{10}$
	1.64	260	3,212	8.58	20	0.053	25.41	1.75	$6.21 \cdot 10^{10}$
	1.64	260	3,180	3.51	29.8	0.033	17.06	1.75	$6.75 \cdot 10^{10}$
	1.64	260	2,230	2.13	39.8	0.026	12.77	1.75	$6.35 \cdot 10^{10}$
	1.64	260	3,354	1.08	56.0	0.018	9.08	1.75	$6.57 \cdot 10^{10}$
Nitric Oxide.	1.64	260	3,311	682.3	5.17	0.884	98.24	1.75	$1.45 \cdot 10^{10}$
	1.64	260	3,299	80.3	10.0	0.238	50.81	1.75	$2.78 \cdot 10^{10}$
	1.64	260	3,370	70.6	11.67	0.239	43.56	1.75	$2.37 \cdot 10^{10}$
	1.64	260	3,158	36.12	15.14	0.171	33.58	1.75	$2.55 \cdot 10^{10}$
	1.64	260	3,192	15.36	20.0	0.096	25.41	1.75	$3.45 \cdot 10^{10}$
	1.64	260	3,335	9.64	23.8	0.069	21.35	1.75	$4.05 \cdot 10^{10}$
	1.64	260	3,333	5.09	32.0	0.044	15.89	1.75	$4.69 \cdot 10^{10}$
	1.64	260	3,335	3.12	37.4	0.035	13.58	1.75	$5.07 \cdot 10^{10}$
	1.64	260	3,378	1.84	44.6	0.024	11.39	1.75	$6.10 \cdot 10^{10}$
	1.64	260	3,294	1.43	50.2	0.022	10.12	1.75	$6.05 \cdot 10^{10}$
Oxygen.	1.64	260	3,196	28.08	5.46	0.048	93.06	1.75	$2.55 \cdot 10^{11}$
	1.64	260	3,220	5.02	10.21	0.016	49.78	1.75	$4.08 \cdot 10^{11}$
	1.64	260	3,174	4.55	10.82	0.016	46.97	1.75	$3.95 \cdot 10^{11}$
	1.64	260	3,227	1.38	16.2	0.007	31.37	1.75	$5.90 \cdot 10^{11}$
	1.64	260	3,270	0.49	24.0	0.004	21.18	1.75	$7.64 \cdot 10^{11}$
Nitric Oxide.	3.873	238	6,794	1.417	8.26	1.425	57.77	0.94	$5.06 \cdot 10^{10}$
	3.698	238	8,991	1.354	10.81	1.416	44.12	0.78	$6.83 \cdot 10^{10}$
	3.873	238	13,630	699.3	12.85	0.627	37.14	0.90	$8.45 \cdot 10^{10}$
	3.954	238	16,150	463.1	14.56	0.406	32.77	0.89	$12.03 \cdot 10^{10}$
	3.954	238	16,080	336.2	14.23	0.292	33.54	1.00	$12.01 \cdot 10^{10}$
Hydrogen Sulphide.	3.873	238	8,932	454	11.31	0.548	42.20	1.33	$3.45 \cdot 10^{10}$
	4.227	238	10,560	867	14.45	1.095	33.02	0.94	$3.91 \cdot 10^{10}$
	4.613	238	9,999	1.543	12.77	1.705	37.38	1.00	$2.45 \cdot 10^{10}$
Sulphur Dioxide.	3.104	238	1,401	0.806	3.66	0.021	130.4	1.52	$1.69 \cdot 10^{13}$
	3.104	238	1,473	0.974	3.69	0.024	129.3	1.60	$1.25 \cdot 10^{13}$
Sulphur Trioxide.	3.954	238	1,237	1.243	3.38	0.034	141.3	1.10	$2.28 \cdot 10^{13}$

zone caused a marked decrease in the intensity of the light re-emitted from the sodium atoms in the tube—a process entirely analogous to the quenching of resonance radiation. This we have observed in many cases to be a prelude to the formation of a stable flame at higher carrier gas pressure, and indicates some relationship between quenching and chemical reaction.

Water Vapour.—No reaction between water vapour and sodium vapour was observed for nitrogen pressures from 2 to 10 mm. Furthermore, under these conditions no indication of quenching of the sodium resonance radiation was observed.

Carbon Dioxide.—At 3 mm. nitrogen pressure carbon dioxide did not react. Increase of the carbon dioxide pressure or of the nitrogen pressure produced only a slight quenching and even at 13 mm. nitrogen pressure no

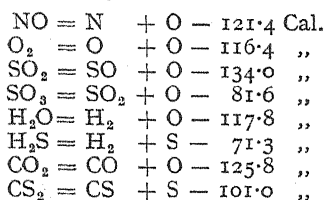
reaction flame was obtained. It is possible that reaction may occur at higher inert gas pressures.

Hydrogen Sulphide.—This gas behaved differently from either water vapour or carbon dioxide. At low pressure of nitrogen (3 mm.) the effect of the hydrogen sulphide was purely a quenching action. At higher pressures of nitrogen (10 mm.) a stable reaction flame was obtained, and a few observations in the range 10–14 mm. nitrogen showed that the reaction rate depended on the carrier gas pressure as with oxygen and nitric oxide (Table I).

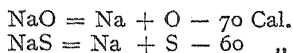
Sulphur Dioxide and Sulphur Trioxide.—Both of these gases showed remarkable reactivity towards sodium atoms (Table I). A typical reaction flame was obtained at 3 mm. nitrogen pressure. It was not possible to study the pressure dependence of the reaction velocity in these cases, since the reactions occurred with a collision efficiency of 1/10 which is outside of the limit (1 in 50) to which the method may be used for quantitative results.

Carbon Disulphide.—This gas has been previously studied by Heller and Polanyi,⁶ and the result is included here for comparison. They find a reaction velocity constant of 3.1×10^8 c.c. Mole⁻¹ sec⁻¹, and interpret the reaction as taking place by a triple body collision mechanism.

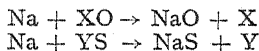
Thermochemical Considerations and Reaction Mechanism.—Using the following dissociation energies



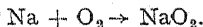
in conjunction with the energies of dissociation of NaO⁷ and NaS,⁸ viz. :



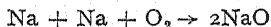
it is evident that all possible reactions of the type



are considerably endothermic.* It may be concluded, therefore, that the observed reactions with sodium atoms cannot take place by bimolecular metathesis. It seems that the only possible reaction is an association reaction of the type



Our kinetic studies show that this may occur either by a termolecular reaction in which the carrier gas serves as a third body or as a bimolecular reaction, the actual order which the reaction follows being determined by the pressure of the carrier gas. Reactions of the type



are excluded, since they would correspond to reaction rates much smaller than those found.

⁶ Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 639.

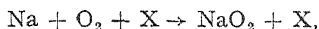
⁷ See previous paper, page 1575.

⁸ This was taken as the mean of $D_{\text{S}_2} = 101$ cal and $D_{\text{Na}_2} = 18$ cal.

* The inaccuracy of the heat of dissociation of NaO and NaS might permit a variation of 10 cal. in the endothermicity. Since all the reactions with the exception of H₂S and SO₃ are endothermic to the extent of at least 30 cal., this inaccuracy cannot modify the above conclusion. The experimental results with H₂S and SO₃ indicate that the mechanism in these cases is the same as that for the other compounds studied.

Reaction Kinetics.

Up to the present a detailed investigation of the pressure dependence of the reaction rate has been made only for the reactions of oxygen and nitric oxide. These results are plotted in Fig. 3. At low pressures the reaction velocity constant varies almost linearly with the pressure, an observation previously made by Haber and Sachse⁹ for the reaction of atomic sodium with oxygen. These authors did not observe the change of slope of the curve at higher pressures, since the maximum pressure they employed was 10 mm. of carrier gas. They interpreted their observations as occurring via a termolecular reaction . . .



where X acts as a third body to carry off the energy of the reaction. This we have confirmed at low carrier gas pressures but at high pressure the reaction changes over to a simple bimolecular mechanism. Treating the general case of a termolecular reaction, the reaction may be considered as taking place in the following stages :

- (1) $\text{Na} + \text{X} \rightarrow \text{NaX}^* \quad k_1$
- (2) $\text{NaX}^* \rightarrow \text{Na} + \text{X} \quad k'_2$
- (3) $\text{NaX}^* + \text{Y} \rightarrow \text{NaX} + \text{Y} \quad k_3$

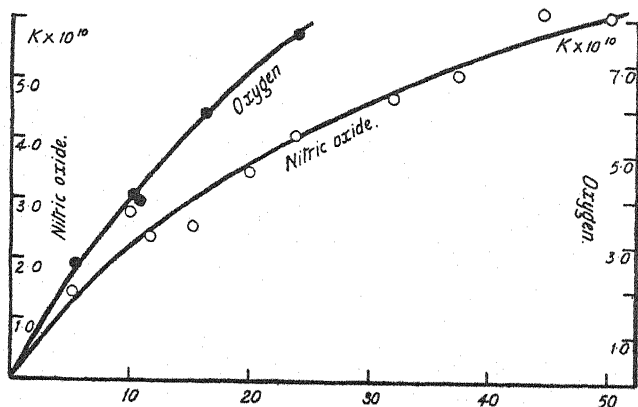


FIG. 3.

where X is the reacting molecule, Y the inert gas, and the asterisk indicates that the molecule possesses the heat of reaction as internal energy. The association reaction (1) gives rise to an unstable complex which may dissociate according to (2) or be stabilised by subsequent collision with a molecule of Y. Let us now consider the meaning of the measured velocity constant k (calculated from equation (1) (page 1572, previous paper) in terms of the velocity constants k_1 , k'_2 and k_3 . The rate of loss of sodium will be given by

$$-d\text{Na}/dt = k_1 p_{\text{Na}} p_{\text{X}} - k'_2 p_{\text{NaX}^*} \quad (4)$$

and the rate of change of concentration of the NaX^* molecules by

$$-d\text{NaX}^*/dt = k_1 p_{\text{Na}} p_{\text{X}} - k'_2 p_{\text{NaX}^*} - k_3 p_{\text{NaX}^*} p_{\text{Y}}.$$

In the stationary state the (NaX^*) will be constant, and the above expression will be equal to zero.

⁹ Haber and Sachse, *Z. physik. Chem.*, Bodenstein Festband, 831, 1931.

Solving for p_{NaX^*} and introducing into equation (4), it follows that the loss of sodium is

$$-dp_{\text{Na}}/dt = \frac{k_1 k_3}{k_2' + k_3 p_Y} \cdot p_Y p_{\text{Na}} p_X,$$

and in accordance with the calculation of the formula for k this is equal to

$$-dp_{\text{Na}}/dt = k p_{\text{Na}} \cdot p_X,$$

thus giving the following relationship between k and the individual constants k_1 , k_2 and k_3 :

$$k = \frac{k_1 k_3}{k_2' + k_3 p_Y} \cdot p_Y \quad . \quad . \quad . \quad . \quad . \quad (5)$$

According to this equation, the plot of k against the pressure p_Y should pass through the origin and approach asymptotically the value k_1 at high pressures of Y . This trend was confirmed in our experiments (Fig. 3) in which the measured velocity constant k is plotted against the total pressure in the reaction vessel. Unfortunately, it was not possible to use pressures

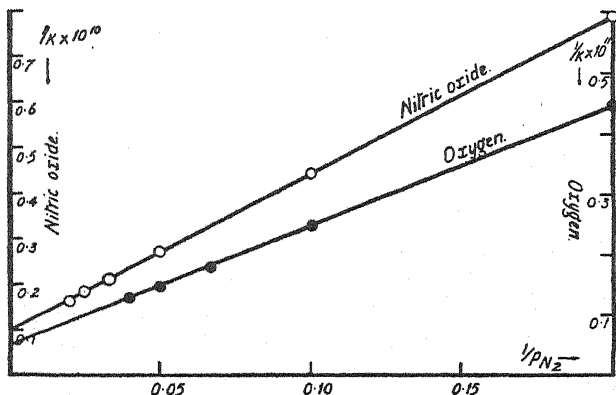


FIG. 4.

of nitrogen high enough to obtain k_1 from the asymptotic limit of the curve, but this may be done in the following way. Inverting equation (5),

$$\frac{1}{k} = \frac{k_2'}{k_1 k_3} \cdot \frac{1}{p_Y} + \frac{1}{k_1} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

it is seen that if the proposed mechanism is followed, then the plot of $1/k$ against $1/p_Y$ where p_Y is the total pressure in the reaction vessel, would be a straight line. This is found to be the case for both the reaction of oxygen and nitric oxide (Fig. 4). It follows from (6) that the intercept of the line on the $1/k$ axis is $1/k_1$ and the slope of the line is equal to the factor which, together with a knowledge of k_1 , gives the value of k_2'/k_3 . The values of k_1 and k_2'/k_3 obtained in this way are given in Table II.

TABLE II.

Reaction.	k_1 , c.c. mol. ⁻¹ sec. ⁻¹ .	$\frac{k_2'}{k_3}$, mol. c.c. ⁻¹ .	k_2' , sec. ⁻¹ .	τ , sec.	K , mol. ⁻¹ c.c.
Na NO	$1 \cdot 10^{11}$	$1 \cdot 10^{-6}$	$4 \cdot 10^8$	$3 \cdot 10^{-9}$	$2 \cdot 5 \cdot 10^2$
Na O ₂	$2 \cdot 10^{12}$	$1 \cdot 2 \cdot 10^{-6}$	$4 \cdot 8 \cdot 10^8$	$2 \cdot 10^{-9}$	$4 \cdot 2 \cdot 10^2$

We can evaluate k_2' if we assume that every collision between the unstable complex and the nitrogen molecule is effective in stabilising the complex. Using a collision diameter of 5×10^{-8} cm., k_3 equals 4×10^{14} c.c. mol.⁻¹ sec.⁻¹. This leads to the values of $\tau \left(= \frac{1}{k_2'} \right)$ of about 10^{-9} sec. (Table II) for the complexes NaO_2^* and NaNO^* . If k_3 is less than corresponding to every collision leading to the transfer of energy, then the calculated value of τ becomes still larger. On the other hand, if reaction (3) occurs with enhanced collision diameters, then τ comes out to be smaller than 10^{-9} . We hope to obtain further information about k_3 by using other carrier gases.

Discussion.

We shall consider first the velocity constants k_1 and k_2' . The normal states of the oxygen and nitric oxide molecules are $^3\Sigma'$ and $^2\Pi$ respectively, the sodium atom 2S and that of the complexes NaO_2 and NaNO are doublet and single states respectively; the reactions of oxygen and nitric oxide with sodium takes place, therefore, with a change of multiplicity of state and the reaction rate will therefore be determined by a transition probability between two states of the system, i.e., by the probability of the molecules getting from a higher to a lower potential energy surface. The probability of this transition, which will appear as a restriction in the expression for the velocity of the reaction, can be estimated from the experimental results (Table II.).

Much more information may be obtained from a knowledge of the equilibrium constant between the initial and the final state of the reaction. Two cases must be distinguished, (a) when the reaction rate is determined by a transition probability of the above type the restriction will be the same in both directions and will not occur in the equilibrium constant, and (b) when the steric factor is determined by the reduced probability of the collided state independent of transition probabilities. In such cases this reduced probability will be included in the equilibrium constant, a knowledge of which and of either the velocity constant of the forward or reverse reaction will then suffice to evaluate the velocity constant of the opposing reaction.

The equilibrium constant between the initial and final state of the reaction $A + B \rightarrow AB$ can be calculated statistical mechanically and is equal to

$$K = \frac{C_{AB}}{C_A C_B} = \frac{f_{AB}}{f_A f_B} e^{Q/RT} = \lambda e^{Q/RT} \quad (7)$$

where f_{AB} , f_A , f_B are the complete partition functions of the molecules AB , A and B respectively and Q is the heat of reaction.

The equilibrium constant $K = k_1/k_2$ where k_1 and k_2 are the velocity constants of the bimolecular association and unimolecular dissociation respectively and are defined according to the following equation if we assume that the association reaction requires no activation energy:

$$\begin{aligned} -d(C_A + C_B)/dt &= k_1 C_A C_B = p Z C_A C_B, \\ \text{and} \quad -dC_{AB}/dt &= k_2 C_{AB} = p A e^{-Q/RT} \cdot C_{AB} \end{aligned}$$

where p is the restriction imposed by the transition and will be the same for both reactions.

Now the equilibrium constant determined from the experimental reaction velocities (Table II) is not K but that between the initial state

(A and B) and a state in which the complex formed still possesses its energy of formation Q , *viz.*,



and

$$K' = (C_{AB})_Q / C_A C_B = \frac{k_1}{k_2} \quad . \quad . \quad . \quad (8)$$

k_1 is defined as above but k_2' is now given by

$$-d(C_{AB})_Q/dt = k_2'(C_{AB})_Q.$$

but

$$(C_{AB})_Q = C_{AB} e^{-Q/RT} \cdot f(Q, s) \quad . \quad . \quad . \quad (9)$$

where $f(Q, s)$ is determined by the internal energy of the complex Q and the number of degrees of freedom of vibration s .

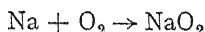
Hence from (8) and (9)

$$\begin{aligned} K' &= C_{AB} / C_A C_B \cdot e^{-Q/RT} \cdot f(Q, s) \\ &= K \cdot e^{-Q/RT} \cdot f(Q, s), \end{aligned}$$

and therefore from (7)

$$K' = \lambda \cdot f(Q, s).$$

Now λ can be estimated directly from the partition function of the molecules A, B and AB. We estimate that λ for the reaction



assuming that the molecule NaO_2 is non-linear ($\theta = 120^\circ$) with moments of inertia 7.47×10^{-39} , 14.6×10^{-39} , 22.15×10^{-39} c.g.s. and fundamental frequencies ν_1 , ν_2 and ν_3 equal to 1100, 600, 1300 cm^{-1} respectively, is approximately equal to $1.0 \text{ mol}^{-1} \text{ c.c.}$ The $f(Q, s)$ can be calculated from classical statistical mechanics¹⁰ and to give by

$$f(Q, s) = \left[\frac{1}{(s-1)!} (Q/RT)^{s-1} + \dots + 1 \right].$$

For molecules of the type NaO_2 and NaO , $s = 3$ and taking the strength of the NaO bond (p. 1591) as 40,000 to 50,000 Cal., this factor is equal to approximately 10^3 so that $K' = 10^3 \text{ mol}^{-1} \text{ c.c.}$ which is in good agreement with the experimental results (Table II.).

But
$$K' = \frac{k_1}{k_2} = \frac{pZ}{pA} = 10^3 \text{ mol}^{-1} \text{ c.c.} \quad . \quad . \quad . \quad (10)$$

The bimolecular collision number Z calculated in the usual way equals $4 \times 10^{14} \text{ c.c. mol}^{-1} \text{ sec}^{-1}$ when $p = 1$ and introducing this in (10) it is seen that $A \sim 4 \times 10^{11} \text{ sec}^{-1}$.

Now the lifetime of the complex of the type NaO_2 ($1/A$) has been computed by Rosen¹¹ by quantum mechanical methods and recently by Kimball¹² using the classical vibration theory. According to the calculation of the latter author we should expect A to be about 10^{11} to 10^{12} sec^{-1} if the bond breaking is of the order of 50,000 Cal. which is in good accord with the calculated value of A assuming $p = 1$. A similar result is obtained if we use the statistical mechanical method of Kassel¹³ for estimating the lifetime of the complex.

¹⁰ Hinshelwood, *Kinetics of Chem. Change in Gaseous System*, 2nd ed., Oxford Press.

¹¹ Rosen, *J. Chem. Physics*, 1933, 1, 319.

¹² Kimball, *ibid.*, 1937, 5, 310.

¹³ Ref. 1, page 44.

If we introduce the factor $p = 10^{-2}$ to 10^{-3} to take account of the transition probability then $A = 10^8$ to 10^9 . The same factor will occur in the association reaction and thus $k_1 = 10^{12}$ to 10^{13} c.c. mol.⁻¹ sec.⁻¹. This excellent accord between the theoretical and experimental values of the ratio k_1/k_2 assuming that the rate is determining by a transition probability shows that the additional factor (for instance, that determining the geometric condition of the collision) in k_1 must be small. This agrees with the general theory of the steric factor as shown by the following considerations.

The nature of the complete steric factor has been discussed recently in terms of the transition state,¹⁴ and it has been shown that the reaction of an atom and a molecule in which two degrees of freedom of translation in the initial molecule pass over into two degrees of freedom of vibration in the transition state does not give rise to a large steric factor, e.g., the reaction $\text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I}$ has been found to have a steric factor of unity. This additional factor will cause then only a slight decrease in the above value for k_1 .

The agreement of theory and experiment in the foregoing calculation is only obtained by making the assumption that the activation energy of reaction k_1 was zero or very small. It is desirable therefore, not only to generalise the theory for the case in which k_1 does have an activated energy but also to enquire how the above conclusions would be modified if this were the case.

Carrying through the calculation as before, the experimentally determined equilibrium constant K^* is now that between the molecules in their initial states and those in energy state in which the molecules formed have an internal energy $E + Q$ where E is the activation energy of k_1 and Q is the heat of reaction. Thus

$$K^* = (C_{AB})_{E+Q} / C_A C_B$$

$$= K \cdot (C_{AB})_{E+Q} / C_{AB}$$

where

$$k = C_{AB} / C_A C_B = \lambda e^{Q/RT}$$

But

$$(C_{AB})_{E+Q} = C_{AB} f(E, Q, s) e^{-(E+Q)/RT}$$

and therefore

$$K^* = K \cdot f(E, Q, s) e^{-(E+Q)/RT} \\ = \lambda \cdot e^{-E/RT} f(E, Q, s).$$

Comparing this expression with that obtained when $E = 0$, viz., $K' = \lambda \cdot f(Q, S)$ it is seen that the principal difference is the term $e^{-E/RT}$. The function $f(E, Q, S)$ is now

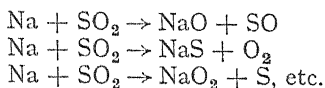
$$\left[\left(\frac{1}{s-1} \right) ! \left(\frac{E+Q}{RT} \right)^{s-1} + \dots + 1 \right]$$

and unless E is very high this does not differ by more than a small factor from $f(E, Q)$ if $s = 3$ and $Q = 40,000$ to $50,000$ Cal.; for example, with $Q + E = 40,000$ and $Q + E = 50,000$ Cal. the value of the above function is 700 and 1100 respectively. On the other hand the exponential term is very sensitive to E and thus if $E = 10,000$ this is equal to 10^{-3} . Such a value for E would cause a striking disagreement with the experimental result. These results can only be explained if E is small, i.e., k_1 probably requires an activation energy* of less than 2000 Cal.

¹⁴ Eyring, *J. Chem. Physics*, 1935, **3**, 107; Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; Bawn, *ibid.*, 1935, **31**, 1536.

* Recent experiments with nitric oxide carried out at two temperatures justify this conclusion. These experiments indicate a slightly negative temperature coefficient for the reaction of nitric oxide. It is fairly certain that the reaction has no appreciable activation energy.

The reactions of sodium atoms with sulphur dioxide is particularly interesting since they provide a means of estimating the life of the complex. It is certain that the metathesis reactions



are strongly endothermic, and therefore the only possible reaction is the bimolecular association process. This proceeds at almost every collision of the particles (Table I, bottom section) and the lifetime of the associated complex must in this case be long enough to ensure that every complex formed experiences at least one collision with the nitrogen during its lifetime. At a total pressure of 3 mm. this time is of the order 10^{-9} to 10^{-10} sec. Now this is the order of the lifetime expected according to the theories previously discussed for molecules with $s = 6$ if the bond formed is not too weak. It appears then that in this case the reaction rate is not determined by a transition probability as with NO, etc. It does not seem unreasonable to expect a different mechanism in these two cases when we consider that O_2 and NO simulate free radicals in their chemical behaviour in contrast to the fully saturated molecule like sulphur dioxide.

Nature of the Associated Molecule.

In order to account for the lifetime of the associated complex, it was necessary to assume that the sodium atom formed with the interacting molecule a bond of considerable strength. It is important, therefore, to enquire further into the exact nature of this complex. Both the normal oxygen ($^3\Sigma$) and nitric oxide ($^2\Pi$ state) are paramagnetic gases, the former since two electrons are unpaired in the molecule whilst the latter possesses an unshared electron. There is no difficulty for one of the unpaired electrons in these molecules to pair up with the electron of the sodium atom giving rise to the formation of a normal type of valence bond. Much experimental evidence exists which seems to indicate that molecules of this type are readily formed. Zintl and Harder¹⁵ have shown that NO reacts with sodium in liquid ammonia to give sodium nitrosyl NaNO, which can be filtered off as a whole solid. The corresponding compound HNO or $(\text{HNO})_x$ is formed when hydrogen atoms¹⁶ react with NO at low temperatures. The formation of HO_2 by the reaction of H and O_2 has been assumed to play an important rôle in such varied types of reaction as the photochemical reaction of H_2 and O_2 , the hydrogen-chlorine combination inhibited by O_2 and the catalytic decomposition of H_2O_2 in solution. Neumann¹⁷ has recently shown that potassium peroxide KO_2 is formed when O_2 is passed over potassium at 300° . This substance is highly coloured and paramagnetic in conformity with its chemical formula KO_2 . Bodenstein and Schenck,¹⁸ from a study of the inhibition of the H_2 - Cl_2 reaction by O_2 estimated the energy of formation of HO_2 from H and O_2 as 44 Cal. Haber and

¹⁵ Zintl and Harder, *Ber.*, 1933, **66**, 578.

¹⁶ Harteck, *ibid.*, 423.

¹⁷ Neumann, *J. Chem. Physics*, 1934, **2**, 31.

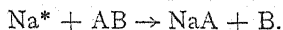
¹⁸ Bodenstein and Schenck, *Z. physik. Chem.*, B, 1933, **20**, 420.

Weiss¹⁹ gave a value 50 Cal. from the catalysed decomposition of H_2O_2 and provisional quantum mechanical calculation leads to a value of about 60 Cal. It appears reasonably certain that the $\text{H}-\text{O}_2$ bond is of the order of 50 Cal.; the NaO_2 bond will be slightly weaker than this and we may assume a provisional value of 40 Cal. On the other hand it is not so obvious how the saturated molecules H_2S , SO_2 , etc. form stable complexes. Calculations, using the London's equations, show that such complexes are not formed by the operation of the so-called van der Waals' forces, since this leads to a binding energy much too low. It is necessary to assume the formation of a valence bond as with O_2 . This type of molecule formation can only occur by the fissure of a s^2 or a p^2 group of electrons in the molecule. The condition of reaction then is determined by the condition that this is energetically possible by the attack of a sodium atom.

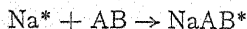
Quenching of Sodium Fluorescence.

It was observed that O_2 , NO , H_2S and CO_2 at low pressures of carrier gas caused a noticeable quenching of the sodium resonance light. (It should be explained that the method of observing the flame is to excite by means of a sodium resonance lamp some of the sodium atoms in the flame. These atoms then re-emit the D line and the reaction zone appears as a small spherical flame. The number of these atoms excited is only a small fraction (10^{-8}) of the total number present in the reaction zone, and it should therefore be emphasised that the reaction measured is that of the normal sodium atoms and not those in the excited state. The actual quenching action observed at low pressures is naturally concerned with this small concentration of sodium atoms.) It was found that the quenching action at low pressures of carrier gas was generally followed by chemical reaction at higher gas pressures. It appears then that there is some analogy between quenching and true chemical reaction. Both processes belong to the general problem of collisions. The chemical change in these experiments is known to be a direct association reaction whereas the quenching may take place by either of the following processes: (a) the exchange of excitational energy of the sodium to the colliding particle either in the form of electronic energy or as translational or vibrational energy; (b) by direct chemical interaction between the excited atom and the gas which is quenching.

The latter processes may occur either by the transfer of the excitational energy of the sodium atom to the colliding particle which may be dissociated or by chemical reaction with the particle, such as



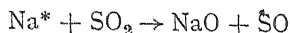
This mechanism of the quenching processes has been given by Kondratjew and Siskin²⁰ for a number of diatomic gases; they find that large cross-sections for quenching correspond to exothermic reactions of the above type. However, our kinetic studies suggest that there is an alternative mechanism—the direct association.



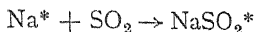
¹⁹ Haber and Weiss, *Proc. Roy. Soc., A*, 1934, 147, 332.

²⁰ Kondratjew and Siskin, *Physik. Z. Soviet Union*, 1935, 8, 644.

besides the metathesis. This seems to be the case with sulphur dioxide for which the reaction



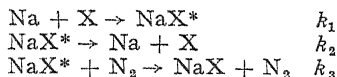
is slightly exothermic. The association reaction



by analogy with our experiment may be very fast. The measurement of the quenching cross-section of this gas would be interesting.

Summary.

The reactions of sodium atoms with NO, O₂ and other oxides and sulphides have been shown to occur according to the following mechanism:



The velocity constant k_1 and the ratio k_2/k_3 have been determined. It is concluded that at high nitrogen pressures the reactions are bimolecular, whilst at low pressures the rate is determined by a triple body collision mechanism. A general theory of these reactions is given, and it is concluded that k_1 for Nitric Oxide and Oxygen is determined by a transition probability.

The authors wish to express their thanks to Professor M. Polanyi for his constant advice and encouragement throughout the investigations described in this and the previous paper. One of them (A. G. E.) wishes to express his indebtedness to the Department of Scientific and Industrial Research for a Grant.

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REVIEWS OF BOOKS.

Electricity and Magnetism for Degree Students. By S. G. STARLING
London: Longmans, Green & Co., 1937. Pp. 630. Price 12s. 6d. net.

Mr. Starling's treatise is too well-known to need any detailed description. In this, the sixth edition, the author has had to excise certain matters, which, as he holds, have become of minor importance, in order to provide space for the discussion of the latest developments in atomic physics. Whether this is desirable in a work which is predominantly classical in outlook is a matter of opinion, but it would seem that the more appropriate method is to develop the major themes of atomic physics in a work specially devoted thereto.

The book may be used with profit by any student of degree standard, and a student aiming at Special Honours will find that a close study of the book will give him a good grounding in the classical advanced works. In this edition, as in the earlier editions, will be found excellent expositions of the theory and practice of alternating currents, of Maxwell's field equations, and of the standard methods for the measurement of inductance and of capacitance. Alike as a textbook and as a handy book of reference,

the work can be strongly recommended ; it should have a long and useful life before it in its new form.

The author is reserved in his expressions of praise or blame, but it would appear that he does not altogether approve of the substitution of *Oersted* for *Gauss* as the name for the unit of intensity of magnetising field, and of the use of *Gauss* to denote the unit of magnetic induction or flux-density.

A. F.

Applications of the Method of Symmetrical Components. By WALDO V. LYON. London: McGraw Hill Publishing Co. Ltd., 1937. Pp. 579. Price 36s. net.

A brilliant colloid chemist who started life as mathematician and engineer once remarked to the writer that there was nothing that he had studied, from the Heaviside calculus to Chinese metaphysics that did not, sooner or later, find an application to colloid science.

The method of symmetrical components, the development of which is based on a study of the operation of induction motors under unbalanced conditions, may seem remote from those studies which occupy the minds of the physical chemists of to-day. But one never knows. The induction motor is linked with physical optics ; a stationary sinusoidally distributed field is equivalent to two equal and constant sinusoidal fields moving with equal and opposite angular velocities, and there is a close analogy between this concept and the Fresnel analysis of a plane polarised beam into two opposite circularly polarised beams.

Whether other analogies do or do not arise, every student of physical science who is interested in the use of mathematical methods as a tool for the elucidation of physical problems will find in Professor Lyons' authoritative and elegant discussion of induction machines, transformers, power networks and transmission lines matter of absorbing interest.

Great institutions often have small and almost unnoticed beginnings. It is worth while to recall that the induction motor, "a dominating factor in the distribution of electric energy," takes its origin from a meeting of the Physical Society of London at which Mr. Walter Baily exhibited a rudimentary motor on the occasion of his reading a paper entitled "A mode of producing Arago's rotations."

A. F.

The Alloys of Iron and Carbon. Vol. I., Constitution: S. EPSTEIN (xii + 476 pp., 30s. net). Vol. II., Properties: F. T. SISCO (xiii + 777 pp., 45s. net). (London: McGraw-Hill Publishing Co., Ltd., 1937.)

These two volumes, together with the one dealing with the metal iron itself, published some little time ago, form, in effect, the basis of the series of the monographs on "Alloys of Iron" which are being prepared with such care and thoroughness by the Iron Alloys Committee of the Engineering Foundation (U.S.A.) under the able chairmanship of Prof. G. B. Waterhouse, of the Massachusetts Institute of Technology. They deal fundamentally with the properties of iron-carbon alloys, as free as possible from all other metals or non-metallic impurities, but, in addition, they cover the constitution and properties of ordinary carbon steels which contain certain impurities and sufficient additions of metals such as silicon,

manganese and aluminium to enable a commercially sound product to be obtained but which are not commonly regarded as alloy steels.

High purity alloys, though more or less laboratory curiosities, are of great interest to the metallurgist as they form a base on which to build up data regarding the effect of alloy additions; they also supply a clue to the properties of the really "pure" iron-carbon alloys which have not yet been prepared and possibly never will be, but which are of fundamental scientific importance.

After a general introduction, the author of Vol. I. deals in three chapters with the iron-iron carbide diagram. He surveys critically the data obtained by various investigators as to the position of phase changes and finally by judicious weighting and averaging of selected values arrives at a probable form of the diagram, which in the absence of more completely satisfying data, is probably more nearly right than any other which has been suggested. Possibly the position of the solidus for carbon contents between about 0.2 and 1.7 per cent. is less certain than any other line in the diagram with the exception of the solubility of Fe_3C in molten iron. Most of the values for this part of the solidus fall into two groups, giving respectively a [practically straight line (as in Carpenter and Keeling's 1904 diagram) and a line strongly convex to the carbon ordinate. After weighing all the evidence, the author decides in favour of the former and while one may agree that such a line may more nearly represent equilibrium conditions than the other, many metallurgists would consider it dangerous to regard 1250° and 1200° C. as the lowest temperatures at which burning would occur in steels containing 1.25 and 1.5 per cent. carbon respectively.

The author considers the application of thermodynamic methods to the iron-iron carbide diagram, but points out that such methods have a very limited application in view of the uncertainties of the available thermal data and of the inexactitude with which the alloys conform to the laws of ideal solutions. Attempts have been made to determine the form in which carbon exists in steel. Calculations based on the lines marking the separation of ferrite or of cementite from austenite do not enable this question to be settled; there is too little difference between the lines calculated for carbon and for Fe_3C to decide this. There is some evidence, however, from calculations based on the liquidus, that carbon in molten alloys exists as Fe_3C .

The author next deals with the iron-graphite diagram which must be regarded as the stable form if the evidence which indicates that cementite is thermodynamically unstable at all temperatures, be accepted as correct. A selected iron-graphite diagram has been drawn conforming to the usual type. As the author remarks, however, there is little clear-cut proof that temperatures and compositions in the iron-graphite system differ markedly from those in the iron-cementite system.

The iron-cementite diagram indicates equilibrium conditions—as nearly as can be obtained—and though these are important, much of the usefulness of steels depends on structural conditions which have little relation to equilibrium. Hence the next few chapters deal with arrested transformations which underlie hardening, changes on tempering, the general macrostructure and microstructure of iron and steel, the effect of mass and furnace atmosphere in heat treatment, the operations of quenching, tempering and carburising, inhomogeneities in commercial

steels and irons, and lastly with factors affecting the quality of Fe-C alloys. These chapters are well handled though one could criticise some of the details. One of the author's main difficulties in writing these chapters must have been to condense the enormous mass of data which has been published during even the last twenty years or so.

A similar difficulty, but in even greater degree, presented itself to Mr. Sisco in dealing with the properties of iron-carbon alloys. A reference to all published work of importance proved to be utterly impossible, if the book was not to exceed a reasonable size, and hence a careful selection was made of data which could be regarded as reasonably representative. A further factor taken into account was availability, preference being given to papers which could be found at one or more large libraries in the United States. While this may be an excellent choice from the standpoint of the student in that country, it may have disadvantages to those in other countries.

Much of the data refers to hardness and tensile properties and it is summarised in chapters dealing respectively with cast steels, hot worked steels, cold worked steels, heat treated steels, grey and white cast iron and malleable cast iron. Effects of mass, grain size and ageing are considered in another chapter. Special properties are dealt with in further chapters, subjects so treated including repeated stresses, effect of temperature as indicated by short time tests and by creep tests, corrosion, electric, magnetic and other physical properties, and lastly miscellaneous engineering properties such as resistance to impact, damping properties, deep drawing properties, machinability, wear resistance and weldability.

The author's scheme is, thus, comprehensive and great care has obviously been taken to give a representative collection of data regarding the properties of carbon steels under these varying conditions. Some of the more specialised subjects—particularly those which are still of a controversial nature—suffer from condensation, but this is not a matter for surprise as much more space than was available would be required to give a complete account of them. However, the author's aim has been to present a representative statement of the general properties of carbon steels and he has done the job very well. Both he and the author of the first volume have maintained the high standard set in the previous volumes of this series of monographs, which make them such a useful addition to the metallurgist's and engineer's libraries.

The Newer Alchemy. By LORD RUTHERFORD. Cambridge: at the University Press, 1937. Pp. viii + 67. Price 3s. 6d. net.

Ars est celare artem; and the present little volume, which is an expansion of the matter of the Henry Sidgwick Memorial Lecture, exhibits all those properties of simplicity and clarity which Lord Rutherford has, so apparently artlessly, at his disposal when he embarks upon a popular exposition of recent advances in physical science.

Anything that comes from his pen on the subject of atomic transformations must command respect; but the question may legitimately be asked: "Is it not difficult, even for the founder of the feast, to tell us something new in this oft-told tale?"

It is difficult; and the author has conquered the difficulty by giving,

during the course of his talk on transformations, artificial and "natural," a simple, adequate and admirably clear account of some of the experimental methods by which the transformations have been brought about. The reader who has perused the little volume—and that difficult fellow, the Intelligent Layman, may read it at a sitting—will not only know what has been done, but should possess a very clear picture of how it has been done. It is no mean feat to have accomplished this double task within the compass of less than seventy pages.

A. F.

The Relativity Theory of Protons and Electrons. By Sir ARTHUR EDDINGTON. Cambridge: at the University Press, 1936. Pp. vi + 336. Price 2rs. net.

Sir Arthur Eddington has carried the story of relativity into a new region. His earlier book on *The Mathematical Theory of Relativity* was concerned with large-scale phenomena and treated matter as continuous. The quantum theory, on the other hand, dealt with atomic and sub-atomic concepts, and Dirac's paper of 1928, which gave the linear wave equation of the electron "made a bridge between quantum theory and relativity theory." This provides the starting-point of the book, which deals with the epoch in which

". . . the intruding one-three-seven,
Had clouded the Newtonian heaven."

The analysis is not easy in the reading, even though much of the mathematical apparatus is explained with Sir Arthur's wonted lucidity; but the interest of the story is compelling, and there is a fascination in following the way in which the values of the fundamental constants of nature tumble out of the analysis—the fine-structure constant $hc/2\pi e^2$ (137), the number N of protons and electrons in the universe ($2 \cdot 136 \cdot 2^{256}$), the ratio of the masses of proton and electron (1847.6, where mass or energy is defined in terms of quantum theory).

It is not impertinent, in either sense of the word, to say that the book is a great contribution to a great subject.

A. F.

Reports on Progress in Physics, Vol. III. The Physical Society. Pp. iv + 394. London, 1937. Price 20s.

There is no preface to these Annual Reports, but if there were, it would no doubt express, in a modified form, those sentiments associated with a well-known broadcast, "We hope to bring you something interesting. . . ." It is quite certain that there is no dearth of interesting subjects, as the present volume shows, for, in addition to continuation reports on basic subjects (Atomic Physics, Heat, Sound, X-rays, etc.), there are special articles on Fluid Motion, the Upper Atmosphere, the Measurement of Noise, Magnetism, Electrical Methods of Counting, Super-conductivity and the Theory of Metals (or should it be Supra-conductivity?) and Photo-electricity.

The reports, which include developments to the end of 1935 and which extend to cover the work of several years in the case of subjects not previously treated in these Reports, are written by acknowledged experts

and are accompanied, in every case, by extensive references to original papers.

Readers of the *Transactions* will find especial interest in the sections on Atomic Physics and the Conservation of Energy and Momentum in Elementary Processes, where there appear discussions on the important subject of nuclear transformations. It would have been an advantage if the same notation had been maintained in these two consecutive articles, and also if the second of them had been more carefully read in proof. The report on Experimental Electricity and Magnetism deals with the modern growth of Debye's theory of polar molecules, while photo-chemistry, the infra-red spectra of the lighter hydro-carbons and the crystal structure of organic and inorganic substances claim attention in other sections.

One cannot but be impressed with the very large amount of information which is collected in the relatively small space of this book and one can only surmise what would be the limited extent of one's knowledge of recent work were it not for the good services of the Physical Society in publishing these annual volumes.

R. H. H.

"The Catalytic Action of Surfaces." By J. E. NYROP. 1937. Copenhagen: Levin and Munksgaard. London: Williams and Norgate. 101 pp. Paper Cover. Price 7s.

The author believes that when a surface adsorbs molecules it does so by ionising them and then attracting the ions formed. Having postulated this the author discusses sundry experimental data from this point of view. The reader's interest in the monograph will depend on his willingness to accept the author's unusual hypothesis.

Protective Films on Metals. Second Edition. By ERNEST S. HEDGES, M.Sc., Ph.D., D.Sc., A.I.C. (Chapman & Hall, 1937. Pp. xv + 397. Price 21s. net.)

A new edition of Dr. Hedges' interesting book will be welcomed by all concerned with Protective Films. In revising the volume, the author's aim has been "not only to bring it up to date, but to increase its usefulness from the industrial viewpoint"; this aim has been fully achieved. The length of the book has been increased by about 40 per cent., and about thirty fresh illustrations have been added. The new matter will be found mainly in the parts dealing with the practical applications of films; indeed the first six chapters, which discuss the scientific basis, have only increased in length by seventeen pages. The chapters dealing with the coatings obtained by electroplating, hot-dipping and cementation, have all been greatly extended, whilst that devoted to sprayed coatings has been almost completely rewritten—a sign of the growing recognition of the practical importance of this method of protection. The former Appendix on paints, lacquers and enamels has now been raised to the status of a Chapter.

All the newly added sections contain a great deal of concisely expressed information regarding recent research work—with references extending up to 1937—and add greatly to the value of the volume. The book should be read by all those interested in the protection of metals—particularly on the practical side. Special attention may be directed to the considerable portions dealing with tin coats and with the anodic behaviour of metals—

subjects with which Dr. Hedges has had close personal contact. The book is well printed, and amply illustrated; the photomicrographs illustrating the structure of tin deposits are clearly reproduced and highly instructive.

U. R. E.

Metallic Corrosion, Passivity, and Protection. By ULICK R. EVANS.
(London, Edward Arnold, 1937. Pp. xxii and 720. Price 45s. net.)

The literature of metallic corrosion is so voluminous, and often so confused, that an authoritative account of the whole subject with its applications is to be heartily welcomed. Dr. Evans has himself contributed largely to this study, and this bulky volume, which replaces the author's well-known smaller work, covers the whole field, and is of the highest interest to both the pure chemist and the practical user of metals. Beginning with a few simple examples, it proceeds by way of surface films, passivity, and tarnishing to the more difficult subjects of corrosion in contact with liquids and of the influence of stress on corrosive action. High-temperature attack, such as the oxidation of heat-resisting steels, is also discussed. The last chapters deal with methods of protection and the testing of protective coatings. A rather unusual arrangement is the division of each chapter into three sections: the scientific basis, the practical applications, and the quantitative treatment where such is possible. The division is not quite logical, and it involves some overlapping and repetition, partly remedied by the provision of a full index. The author disclaims any intention of treating the subject historically, but the chemist who is not a specialist would have liked to see some account of how the theories have developed and how the successive conclusions were reached. The name of Faraday only occurs three times, and then only in passing, whilst other names of importance in the history of the subject are not even mentioned. It would have been interesting to bring out, in a short historical sketch, the fact that certain early ideas have stood the test of time better than their later rivals. However, the present work is not a survey by an outsider, but represents the views of perhaps the most active investigator of corrosion, at the head of a prolific school of research. Dr. Evans, with all his enthusiasm, has striven to be fair to other investigators, and has included a statement by members of the Teddington school of the points on which differences of opinion between them and the Cambridge workers still persist. When the very different conditions of the two sets of experiments are taken into account, it is probable that their reconciliation is not as difficult as has been supposed. The omission of any reference to Vernon's work on page 53 does, however, make the account of the oxide films on iron somewhat misleading.

For the practical man the book is a mine of information, and the critical discussion of methods of protection against corrosion, such as electro-deposition, anodic oxidation, and painting, is of great value. Materials suitable for use in various industries are considered in turn, as well as such subjects as the use of inhibitors in pickling metals, etc. That the index contains the names of 1700 authors is in itself enough to indicate that the labour of compilation must have been very great, and the author is to be congratulated on the completion of a work which will be constantly in the hands of chemists and metallurgists for reference.

C. H. D.

A Textbook of Qualitative Chemical Analysis. By ARTHUR I. VOGEL.
Longmans, Green & Co., 1937. Pp. 383. Price 7s. 6d.

Every enthusiastic teacher feels at some time or another that he would like to write a book giving others the benefit of his knowledge and experience: the work under review clearly represents one of those instances in which the desire has come to fruition. There are available to teachers of chemistry several books on qualitative analysis of both an elementary and an advanced character, but the present book differs in some respects from either extreme and successfully steers a middle course. It is superior to the simpler text-books in the respect that it commences with a section of nearly 100 pages entitled "The Theoretical Basis of Qualitative Analysis." Not only will a student fail to understand completely the processes used in qualitative analysis unless he has a sound knowledge of the underlying principles, but in addition qualitative analysis can be made to form, as this book implies, a very useful and practical approach to a number of important aspects of physical chemistry. The advantage of Dr. Vogel's book over the larger texts is that it frankly does not set out to be a complete treatise on qualitative analysis: the main work is therefore not encumbered by reactions for rare elements, although these are included in a short chapter at the end of the book.

The main scheme of the book follows more or less established lines; the reactions for each of the metals in a group are followed by the appropriate table for their separation from one another. It is gratifying to record that the author has made free use of the organic reagents which have become available in recent years for the detection of a number of metallic ions. A chapter on the reactions of anions follows that on cations, and then comes the most important section of the book from the practical point of view, *viz.*, systematic qualitative analysis, including various dry tests, preliminary tests, and the general scheme for the group separation of metals. This portion is in some senses too comprehensive; for example, there are three alternative methods for the separation of arsenic, antimony and tin, and five different procedures which can be adopted in the presence of phosphates. There does not always appear to be, however, any indication of the advantages and disadvantages of each method. It has been noticed also that the tables given in the earlier parts of the book, intended for use when obtaining practice in the separation of the metals in each group, sometimes differ from those in the later part. On page 171 nickel is separated from cobalt by means of cyanide followed by hypobromite, but on page 296 the ions of the two metals are detected by means of organic reagents without the use of cyanide. In the hands of a teacher who will guide his students along the route for which he has a personal preference this book will prove of great value, and the alternative procedures described will be an advantage. In any case the reader who makes full use of the information given will learn a great deal of chemistry, for all the reactions and separations described are fully and clearly explained. Altogether this book represents a valuable contribution to the teaching of qualitative analysis and those interested in the subject are recommended to give it serious consideration.

S. G.

Ions in Solution. By R. W. GURNEY. Cambridge University Press, 1936. Pp. 206. Price 10s. 6d.

In this book Dr. Gurney attempts an interpretation of the behaviour of electrolytic ions in terms of energy levels, and in his preface expresses the opinion that in this way a step forward may be made for such ions similar to the advance which resulted when Bohr, in 1913, directed attention to the electronic energies of gaseous ions. Familiar processes, as for example the dissolution of a metal and the discharge of an ion, are considered in detail and shown to depend on such factors as the thermionic work function and ionisation potential of the metal, the work required to detach a positive core from it, and the energy of solvation of the ion. These ideas are not new, as may be seen by reference to recent work in electrochemistry, but they have been re-stated and developed with the aid of potential energy curves in such a manner as to harmonise with modern quantum concepts. The logical way in which the author has propounded his theses commands admiration, and every step in his argument is clear and convincing. One of the striking features of the book is that as far as possible phenomena are given physical and mechanical, rather than mathematical, interpretation. For instance, the evolution of heat on dilution of a strong electrolyte at low concentration is generally ascribed to the negative temperature coefficient of the dielectric constant of the solvent: Dr. Gurney goes a stage further and shows that this is connected with the orientation of the solvent dipoles. It is disappointing, however, that so few references to the literature are given: in the 200 pages of text there are not more than a dozen references to original papers—by no means the most important—and nine well-known books are mentioned at the end. Little attempt is made to indicate where the treatment is novel and where it connects, as it frequently does, with well-established aspects of physics and chemistry. In one or two places the opinion of a chemist would have been useful; “chromium dichloride” might pass for chromous chloride (p. 186), but “chromium disulphate” for chromous sulphate is incorrect. The statement (p. 67) that “chemical analysis has had as its main object the removal of each substance from solution . . . in the form of a solid precipitate” or as a gas, does not take into account the vast field of volumetric analysis involving acid-base and oxidation-reduction processes. Apart from the lack of references, the points mentioned above are quite trivial, and Dr. Gurney’s book is undoubtedly one which should be read by all students of electrochemistry: whether the claim made in the preface, referred to at the beginning of this review, will be justified or not remains to be seen. A sequel to the present volume is promised, and its appearance will be awaited with interest.

S. G.

ERRATA (VOLUME XXXIII.), 1937.

Pages 147 and 148. In Figs. 1 and 2, *for* Stannic Chloride *read* Silicon chloride.

Page 163. In the last line of the second group of formulæ, *for* $V_{\alpha_0 M}/\beta_0$, etc., *read* $V^M_{\alpha_0}/\beta_0$, etc.

„ 244. First long paragraph, 7th line, *after* “molecules” *add by footnote*, “See page 267 for a correction of fact, but not of argument.”

„ 251. After the two formulæ between those numbered respectively (7) and (10) *add* the respective numbers (8) and (9).

„ 252. Fifth line, *for* “article 1b” *read* “article 1^(b).”

„ 519. Lines 14-17 should have been placed immediately before the last three lines on page 518.

Pages 592 and 594. The numbered figures are wrongly inserted. Fig. 1 should be numbered Fig. 3 and *vice versa*.

Page 1266. Five lines from bottom, *for* “protophic” *read* “prototropic.”

„ 1268. Line 6, *for* 28·84° C. *read* 24·84° C.

„ 1268. Nine lines from bottom, *for* $p = \Delta S/0.1079$ *read* $p = \Delta \delta/0.1079$.

„ 1270. The line after equation (3) *should read* “and that $V = k_{\text{meas}} \times C_{\text{total nitramide}}$.”

„ 1336. See amplification on page 1362.

„ 1363. Line 6 from bottom, *for* OMoO_4 and OMoF_8 , respectively, *read* OsO_4 and OsF_8 .

„ 1461. Equation (6), and page 1463, Summary, line 8 :—

$$\text{For } TdF_L/dT \text{ read } \frac{TdF_L}{dT}.$$

„ 1461. Footnote 10, and page 1462, Equation (7) :—

$$\text{For } T \frac{dF_V}{dT} \text{ read } \frac{TdF_L}{dT}.$$

„ 1465. Equation (1) :—

$$\text{For } l = \sqrt{\frac{2\eta}{tr \gamma_{LV} \cos \theta}} \text{ read } l = \sqrt{\frac{tr \gamma_{LV} \cos \theta}{2\eta}}.$$

„ 1467. Four lines below formula (3) :—

$$\text{For } \cos \theta, \text{ read } \cos \theta.$$

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